FUNDAMENTAL APPROACH TO LAMINAR FLAME PROPAGATION

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The complete system of equations for a theory of laminar flame equations is presented, taking into account both heat conduction and diffusion, for the case of an arbitrary number of simultaneous reactions. The eigenvalue problem determining the flame velocity is formulated. Two examples are given in order to show that explicit analytical expressions for the flame velocity can be obtained, which are in good agreement with the results obtained by numerical integration of the equations. In the first example (hydrazine decomposition) one reaction is considered as global, i.e., rate-controlling, reaction. In the second example (ozone decomposition) a hypothesis is introduced for the concentration of the free radical O, which corresponds to the steady-state approximation generally used in classical chemical kinetics. In both cases approximate explicit formulae are obtained for the flame velocity using legitimate approximation methods, without making drastic assumptions. The steady-state assumption used for the ozone flame has a bearing on a better understanding of the mechanism of chain reactions in general. The method indicated in the paper gives hope that the more complicated chain reactions, such as the combustion of hydrocarbons, will also be made accessible to theoretical computation.

IT WAS not attempted to give a bibliography for the theoretical studies on laminar flame propagations, since extensive references can be found in the well known books by LEWIS and VON ELBE[1] and by JOST[2], and especially in a survey report prepared by EVANS[3]. Reference will only be made to the work which was undertaken by three groups, to some extent with similar ideas as those presented in this paper. First should be mentioned the group of Russian authors consisting of SEMENOV, ZELDOVICH and FRANK-KAMENETSKY[4]. They assumed that the bulk of the chemical reaction occurs at high temperatures near the adiabatic flame temperature. Based on this assumption, they 'eliminated' the ignition temperature. MILLÁN and the senior author have shown in a paper published jointly[8] that the ' elimination ' means that the computed flame velocity is practically independent of the ignition temperature. Then the work of BOYS and CORNER[5] must be mentioned. The authors think that their methods of approximation are better chosen than those of Boys and Corner. Finally, reference will be

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made to the very elaborate work carried out by HIRSCHFELDER and his collaborators[6,7]. The system of basic equations which this group resolved by numerical integration is identical with that of the authors. In fact, the authors purposely followed Hirschfelder in his assumptions concerning the chemical kinetics data, transfer coefficients, *etc.* in order to show that their method is able to replace laborious numerical operations or series developments.

In the Sections I*A–E* the basic parameters are defined and the basic equations are given. The deduction of the diffusion equations in Sections I*A* and I*D* is especially simple—we believe. Section I*A* giving the laws of the rate of production of species by chemical reaction uses classical chemical kinetics. The mathematical formulation of the problem of laminar flame propagation in Section I*F* is given in full generality for an arbitrary number of reactions. Correspondingly the equations are somewhat overloaded with summations. The reader may restrict his attention to the simple example of one ruling reaction as given in the text. Section I*G* gives some general results which can be obtained from the equations without integrating them. It is pointed out in which case the theorem of constant total enthalpy, obtained first by Semenov, and used as an assumption by Lewis and von Elbe, is really true. Finally Section I*H* compares our mathematical methods with those used by other authors.

Section II deals with the hydrazine and Section III with the ozone decomposition flame. Some summary remarks are contained in Section IV.

I. BASIC EQUATIONS

In a discussion of the fundamental theory of laminar flame propagation it is sufficient to summarize the basic equations for one-dimensional steady flow in reacting gas mixtures. The well known book of CHAPMAN and COWLING[9] may be quoted as a general reference work on the mathematical theory of non-uniform gases for one- and two-component systems. HIRSCHFELDER and collaborators[10] have generalized the studies of Chapman and Cowling for gas mixtures containing an arbitrary number of chemical species. The one-dimensional equations used in the present paper can be derived without difficulty from the general equations. The equation of state for ideal gas mixtures and transport coefficients derived from the classical kinetic theory of gases are used in the present analysis.

Explicit relations for the chemical reaction rates are introduced in a semi-empirical form (*cf* Section I*E*) and no use is made of the theory of absolute reaction rates. It is understood that the fundamental idea of applying reaction rates determined under isothermal conditions in closed vessel experiments to the study of chemical reactions in flow systems is subject to criticism, although it appears that this assumption constitutes a reasonable first approximation for the conditions encountered in laminar flame propagation.

Before proceeding with the presentation of the basic equations, some useful parameters are introduced and the relations between these parameters summarized. The chemical composition in any volume element of the gas stream may be described by the weight fractions $\gamma_1, \gamma_2, \cdots$ of the chemical

species 1, 2, $\cdots$. Similarly, the composition may be defined by the corresponding mole fractions $X_1, X_2, \cdots$. Evidently $\sum_{K=1}^{s} Y_K = \sum_{K=1}^{s} X_K = 1$ where s denotes the total number of chemical species present. The weight fractions and mole fractions are related by the expressions

$$Y_j = \frac{M_j X_j}{\sum_{K=1}^{s} M_K X_K} \qquad \ldots . \quad (1)$$

where M_j is the molecular weight of species j and $\sum_{K=1}^{s} M_K X_K$ represents the average molecular weight, $\overline{M}$, of the gas mixture. In accordance with conventional nomenclature, the number of moles of species j per unit volume is termed the concentration and denoted by the symbol c_j. Evidently

$$c_j = \rho Y_j / M_j \qquad \ldots . \quad (2)$$

where ρ equals the density of the gas mixture. It is then clear that the total number of moles per unit volume, $c_t = \sum_{K=1}^{s} c_K = p/RT$ is related to the density by the expression

$$\rho = c_t \sum_{K=1}^{s} M_K X_K = \frac{p}{RT} \sum_{K=1}^{s} M_K X_K \qquad \ldots . \quad (3)$$

In order to incorporate the principles of chemical kinetics in the expressions for conservation of mass and energy, it is desirable to introduce a third set of parameters, $\varepsilon_j (j = 1, 2, \cdots, s)$. The quantities ε_j are defined in such a way that the difference $m(\varepsilon_j - \varepsilon_{j,0})$ represents the change of mass flow rate of species j per unit area, produced by chemical reaction, between the cross section at which chemical reactions begin (identified by the subscript 0) and an arbitrary cross section which is being considered. The symbol m denotes the constant total mass flow rate through unit area. It is clear that in the absence of diffusion the quantities ε_j and Y_j are identical since, in this case, the change in weight fraction produced by chemical reaction equals the net change in weight fraction. The utility of the set of parameters ε_j becomes evident if the laws of conservation of mass and energy are formulated in terms of ε_j, as is done in Sections I*A* and I*B*.

A. Conservation of mass

Consider the gas volume in a one-dimensional flow problem enclosed between the stations $x = 0$ and $x = x$. Evidently

$$m(Y_j - Y_{j,0}) = m(\varepsilon_j - \varepsilon_{j,0}) + \mathcal{J}_d \qquad \ldots . \quad (4)$$

where $\mathcal{J}_d$ is the diffusion stream of species j into the volume element. In the absence of diffusion at the cross section located at $x = 0$

$$\mathcal{J}_d = -\rho Y_j V_j \qquad \ldots . \quad (5)$$

where V_j is the diffusion velocity of species j. Since $\varepsilon_{j,0} = Y_{j,0}$ it follows from Eqs. (4) and (5) that

$$Y_j - \varepsilon_j = -\frac{\rho}{m} Y_j V_j \qquad \ldots . \quad (6)$$

Let $v = m/\rho$ denote the mass-weighted average velocity of the gas mixture; then Eq. (6) can be written in the equivalent form

$$\varepsilon_j = \Upsilon_j(1 + V_j/v) \qquad \ldots . \quad (7)$$

The net rate of production of mass of species j by chemical reaction per unit volume per unit time will be denoted by the symbol w_j. From the point of view of fluid mechanics, w_j is a source for the j'th chemical species. Utilizing the definition of ε_j it is evident that

$$w_j = m\mathrm{d}\varepsilon_j/\mathrm{d}x \qquad \ldots . \quad (8)$$

The quantity w_j is assumed to be a known function of pressure, temperature and mole fractions. Explicit expressions for w_j will be given in Section I*E*.

B. Conservation of energy

We assume an adiabatic process, neglect viscous forces and also the kinetic energy of the flowing gases because of the assumption of constant-pressure deflagration. In this case there is a balance between the heat flow by conduction and the enthalpy transport. Let us consider again the volume enclosed between the initial and an arbitrary cross section. It was seen above that $m\varepsilon_j = m\Upsilon_j(1 + V_j/v)$ represents the mass flow of the species j produced by chemical reaction. Therefore the enthalpy stream is given by $m\varepsilon_j h_j$ where h_j is the specific enthalpy of the species j. Hence the theorem of the conservation of energy appears in the simple form

$$-\lambda\frac{\mathrm{d}T}{\mathrm{d}x} + m\sum_{j=1}^{s}(\varepsilon_j h_j - \varepsilon_{j,0}h_{j,0}) = 0 \qquad \ldots . \quad (9)$$

The specific enthalpies h_j are known if the specific heats and the heats of formation of the species are known. If the specific heats, $(c_p)_j$, are independent of the temperature, then we may write for the specific enthalpies:

$$h_j = (c_p)_j T + h_j^0 \qquad \ldots . \quad (10)$$

where h_j^0 is the standard specific enthalpy of formation for the j'th chemical species.

In the practical applications it will be assumed that all the $(c_p)_j$ values are equal to the effective average specific heat, $\bar{c}_p$, which is defined by the relation

$$\bar{c}_p = -\frac{\sum_{j=1}^{s}(\Upsilon_{j,f} - \Upsilon_{j,0})h_j^0}{T_f - T_0} = -\frac{\sum_{j=1}^{s}(\varepsilon_{j,f} - \varepsilon_{j,0})h_j^0}{T_f - T_0} \qquad \ldots . \quad (11)$$

i.e.

$$(c_p)_j = \bar{c}_p \quad j = 1, 2, \cdots, s \qquad \ldots . \quad (12)$$

In view of Eqs. (11) and (12), Eq. (9) becomes

$$\frac{\lambda}{m\bar{c}_p}\frac{\mathrm{d}T}{\mathrm{d}x} = (T - T_0) + \sum_{j=1}^{s}(\varepsilon_i - \varepsilon_{j,0})\frac{h_j^0}{\bar{c}_p}$$

Similarly, between the limits T_0 and T_f,

$$0 = (T_f - T_0) + \sum_{j=1}^{s}(\varepsilon_{j,f} - \varepsilon_{j,0})\frac{h_j^0}{\bar{c}_p}$$

Combination of the two preceding expressions leads to the result

$$\frac{\lambda}{m\bar{c}_p}\frac{dT}{dx} = (T - T_f) + \sum_{j=1}^{s}(\varepsilon_j - \varepsilon_{j,f})\frac{h_j^0}{\bar{c}_p} \quad \ldots\ (13)$$

It is now convenient to introduce the following dimensionless parameters:

$$\theta = T/T_f \qquad \theta_0 = T_0/T_f \quad \ldots\ (14)$$

Therefore Eq. (13) can also be written in the form

$$\frac{\lambda}{m\bar{c}_p}\frac{d\theta}{dx} = (\theta - 1) + \sum_{j=1}^{s}(\varepsilon_j - \varepsilon_{j,f})\frac{h_j^0}{\bar{c}_p T_f} \quad \ldots\ (15)$$

As a simple example for the use of Eq. (15) we consider a binary mixture for which $\varepsilon_1 + \varepsilon_2 = 1$ with $\varepsilon_{1,0} = 1$, $\varepsilon_{1,f} = 0$. Hence Eq. (15) becomes

$$\frac{\lambda}{m\bar{c}_p}\frac{d\theta}{dx} = (\theta - 1) + (1 - \varepsilon_2)\frac{h_1^0 - h_2^0}{\bar{c}_p T_f} \quad \ldots\ (16)$$

or, in view of the definition given for $\bar{c}_p$ in Eq. (11),

$$\frac{\lambda}{m\bar{c}_p}\frac{d\theta}{dx} = (\theta - 1) + (1 - \varepsilon_2)(1 - \theta_0) \quad \ldots\ (16a)$$

C. Conservation of momentum

For constant-pressure deflagration the statement that the pressure difference across the flame front is negligible replaces the theorem of conservation of momentum. The conditions under which this assumption is admissible are discussed in reference 12. They are generally fulfilled for laminar flame problems.

D. Diffusion equations

In Section I*A* the diffusion velocity has been shown to be given by the relation

$$-\Upsilon_j V_j = \frac{m}{\rho}(\Upsilon_j - \varepsilon_j)$$

It is now desirable to express V_j in terms of the Υ_j's and ε_j's and of their derivatives.

Consider first the case of a binary mixture. Then for the species $j = 1$

$$-\Upsilon_1 V_1 = \frac{m}{\rho}(\Upsilon_1 - \varepsilon_1) \quad \ldots\ (17)$$

On the other hand, Fick's law for a binary mixture states that[11]

$$V_1 = -D_{1,2}\frac{1}{\Upsilon_1}\frac{d\Upsilon_1}{dx} \quad \ldots\ (18)$$

where $D_{1,2}$ is the binary diffusion coefficient for the interdiffusion of species 1 and 2. Therefore

$$\frac{d\Upsilon_1}{dx} = \frac{1}{D_{1,2}}\frac{m}{\rho}(\Upsilon_1 - \varepsilon_1) \quad \ldots\ (19)$$

For many practical applications it is desirable to replace weight fractions Y_j by mole fractions X_j. From Eq. (1) it follows that for a binary mixture

$$Y_1 = \frac{M_1 X_1}{M_1 X_1 + M_2 X_2}$$

Differentiating this expression with respect to x and taking account of the fact that $X_1 + X_2 = 1$, leads to the result

$$\frac{dY_1}{dx} = \frac{M_1 M_2}{(M_1 X_1 + M_2 X_2)^2} \frac{dX_1}{dx} \quad \ldots . \quad (20)$$

Combining Eqs. (19) and (20) and noting that, according to Eq. (3),

$$\rho = c_t (M_1 X_1 + M_2 X_2)$$

it follows, after some arithmetic manipulations involving Eq. (1) and the relation $\varepsilon_1 + \varepsilon_2 = 1$, that

$$\frac{dX_1}{dx} = \frac{1}{D_{1,2}} \frac{m}{c_t} \left(\frac{X_1 \varepsilon_2}{M_2} - \frac{X_2 \varepsilon_1}{M_1} \right) \quad \ldots . \quad (21)$$

Reference to Eq. (21) shows that in the absence of diffusion transport

$$X_1 \varepsilon_2 / M_2 = X_2 \varepsilon_1 / M_2$$

or

$$M_1 X_1 / M_2 X_2 = Y_1 / Y_2 = \varepsilon_1 / \varepsilon_2$$

This last relation is in accord with the result noted previously that $Y_j = \varepsilon_j$ in the absence of diffusion.

HIRSCHFELDER and his collaborators[13] have shown that one obtains a good approximation for a multicomponent gas mixture with s components by writing for the mole fraction gradient of species j

$$\frac{dX_j}{dx} = \frac{m}{c_t} \sum_{K=1}^{s} \frac{1}{D_{j,K}} \left(X_j \frac{\varepsilon_K}{M_K} - X_K \frac{\varepsilon_j}{M_j} \right) \quad \ldots . \quad (22)$$

where $D_{j,K}$ is the diffusion coefficient for a binary mixture of j and K. Comparison of Eqs. (21) and (22) shows that Eq. (22) is obtained from Eq. (21) formally by replacing the subscript 2 by K and summing over K with the subscript 1 replaced by j.

E. Rate of production of species by chemical reaction[14]

The conservation and diffusion equations given in the foregoing paragraphs determine completely the flow problem with chemical reactions provided chemical kinetics contribute explicit expressions for the rate of production of the various species. In general, we have to consider a number of simultaneous and interdependent reactions, which will be numbered for convenience $r = 1, 2, \cdots$. The r'th reaction is described by the stoichiometric equation

$$\sum_{j=1}^{s} \nu_{j,r}' \mathcal{J} \rightarrow \sum_{j=1}^{s} \nu_{j,r}'' \mathcal{J} \quad \ldots . \quad (23)$$

where the symbol $\mathcal{J}$ denotes the j'th chemical species and $\nu_{j,r}'$ and $\nu_{j,r}''$ represent, respectively, the stoichiometric coefficients of species $\mathcal{J}$ for the reactants and for the reaction products. For example, if O, O_2,

and O_3 represent, respectively, the species $\mathcal{J} = 1$, 2 and 3 in the r'th reaction

$$O + O_3 \rightarrow 2O_2$$

then $\nu_{1,r}' = \nu_{2,r}' = 1,\ \nu_{2,r}' = 0,\ \nu_{1,r}'' = \nu_{3,r}'' = 0,\ \nu_{2,r}'' = 2.$

The 'overall order' of the r'th chemical reaction is

$$n_r = \sum_{j=1}^{s} \nu_{i,r}'$$

The rate of production of the j'th chemical species by the r'th chemical reaction is evidently proportional to the factor $(\nu_{j,r}'' - \nu_{j,r}')$. In the expressions for the rate of production of the s chemical species there occurs a common factor which, according to the classical picture of reaction kinetics, is simply the number of effective collisions producing chemical reactions. It can be computed by application of the 'law of mass action' and is found to be equal to the product of $\prod_{l=1}^{s} (c_l)^{\nu_{l,r}'}$ and a proportionality factor. The proportionality factor is called the specific reaction rate constant (or sometimes simply the rate constant or specific reaction rate). Denoting the specific reaction rate constant, the dimensions of which are sec^{-1} (volume/mole)$^{n-1}$, by k_r for the r'th chemical reaction, we write for the rate of production of moles per unit volume of species $\mathcal{J}$:

$$\frac{dc_{j,r}}{dt} = (\nu_{j,r}'' - \nu_{j,r}')k_r \prod_{l=1}^{s} (c_l)^{\nu_{l,r}'} \equiv (\nu_{j,r}'' - \nu_{j,r}')(R.R.)_r \quad \ldots . \quad (24)$$

where $(R.R.)_r$ represents the rate of reaction for the r'th process.

The specific reaction rate constant is expressed as a function of temperature by the following semi-theoretical expression :

$$k_r = B_r(T/T_f)^{\alpha_r} [\exp(-A_r/RT)] \quad \ldots . \quad (25)$$

Here $B_r\ (T/T_f)^{\alpha_r}$ can be called a 'frequency factor' and has the dimensions sec^{-1} (volume/mole)$^{n-1}$.* The temperature T_f is the adiabatic flame temperature and A_r represents the molar activation energy. With $\alpha_r = 0$, Eq. (25) reduces to the classical Arrhenius law. The collision theory of chemical reaction rates leads to the conclusion that $\alpha_r = 1/2$. In practice the parameters B_r and A_r are determined by fitting the experimental data to Eq. (25) either for $\alpha_r = 0$ or for $\alpha_r = 1/2$.

It is apparent that the source function for the chemical species $\mathcal{J}$, defined by Eq. (8), is

$$w_j = \sum_r w_{j,r} = \sum_r M_j \frac{dc_{j,r}}{dt} \quad \ldots . \quad (26)$$

which becomes, in terms of the rates of reaction,

$$w_j = M_j \sum_r (\nu_{j,r}'' - \nu_{j,r}')(R.R.)_r \quad \ldots . \quad (27)$$

F. Mathematical formulation of the problem of laminar flame propagation

The calculation of laminar burning velocities involves the construction of a stationary flow process starting from the temperature T_0 and a composition $Y_{j,0} = \varepsilon_{j,0} (j = 1, 2, \cdots)$ and ending with the temperature T_f and the

* According to the usual assumptions of classical chemical kinetics, $B_r/T_f^{\alpha_r}$ is a constant for a given chemical reaction and is independent of initial conditions.

composition $Y_{j,f} = \varepsilon_{j,f} (j = 1, 2, \cdots)$. In the one-dimensional problem, the equations of continuity, diffusion and conservation of energy must be satisfied at every cross section. Examination of the number and of the degree of the differential equations shows that a solution can exist only for an eigenvalue of the mass flow rate m[12]. In recent publications on laminar burning velocity[3-8, 12, 14] it has been emphasized that an eigenvalue for m, which is independent of the exact formulation of the cold-boundary condition, is not obtained if an attempt is made to describe laminar flame propagation by a one-dimensional, steady-state process in which the expression for the specific reaction rate given in Eq. (25) remains valid in a premixed gas mixture reaching upstream to infinity. This difficulty is introduced into the physical problem by the mathematical formulation used to describe laminar flame propagation and can be resolved in several ways; for example (*a*) by utilizing as cold-boundary condition a heat sink with a diffusion filter[6,7], or (*b*) by assuming an 'ignition temperature' below which the chemical reaction rates are neglected. In previous publications[8,14] it has been shown that for all ignition temperatures, T_i, somewhat larger than T_0 and somewhat smaller than T_f, practically the same eigenvalue is obtained for m. Hence it will be sufficient for the present purposes to utilize the concept of an ignition temperature when expedient, without entering into an elaborate discussion of the question of appropriate formulation of the cold-boundary condition.

The differential equations describing laminar flame propagation have been given in Eqs. (8), (15), and (22). It is convenient to replace the coordinate x by the reduced temperature θ as independent variable. Therefore we divide Eqs. (8) and (22) by Eq. (15) and obtain the results

$$\frac{d\varepsilon_j}{d\theta} = \frac{\lambda}{m^2 \bar{c}_p} \frac{w_j}{[(\theta - 1) + \sum_j (\varepsilon_j - \varepsilon_{j,f})(h_j^0/\bar{c}_p T_f)]} \quad \ldots . (28)$$

and

$$\frac{dX_j}{d\theta} = \frac{\lambda RT}{c_p p} \frac{\sum_{K=1}^{s} \frac{1}{D_{jK}} \left(X_j \frac{\varepsilon_K}{M_K} - X_K \frac{\varepsilon_j}{M_j} \right)}{[(\theta - 1) + \Sigma(\varepsilon_j - \varepsilon_{j,f})(h_j^0/\bar{c}_p T_f)]} \quad \ldots . (29)$$

where c_i has been replaced by p/RT. According to Eqs. (24) to (27), w_j is given explicitly by the relation

$$w_j = M_j \sum_r \left[B_r \left(\frac{p}{RT_f} \right)^{n_r} \theta^{\alpha_r - n_r} \exp\left(-\theta_r/\theta\right)(\nu_{j,r}'' - \nu_{j,r}') \prod_{l=1}^{s} (X_l)^{\nu_{l,r}'} \right] \quad . . (30)$$

where

$$\theta_r = A_r/RT_f \quad \ldots . (31)$$

and c_j has been replaced by pX_j/RT. Hence Eq. (28) becomes

$$\frac{d\varepsilon_j}{d\theta} = \frac{\lambda M_j}{m^2 c_p} \frac{\sum_r \left[B_r \left(\frac{p}{RT_f} \right)^{n_r} \theta^{\alpha_r - n_r} \exp\left(-\theta_r/\theta\right)(\nu_{j,r}'' - \nu_{j,r}') \prod_{l=1}^{s} (X_l)^{\nu_{l,r}'} \right]}{[(\theta - 1) + \Sigma(\varepsilon_j - \varepsilon_{j,f})(h_j^0/\bar{c}_p T_f)]} \quad \ldots . (32)$$

According to the kinetic theory of gases there is a relation between the thermal conductivity λ and the binary diffusion coefficients $D_{j,k}$ such

that $\lambda\theta/D_{j,k}$ is independent of temperature. For the sake of convenience we shall assume that

$$\lambda = \lambda_f(\theta)1^{-\alpha_r} \quad \ldots . \quad (33)$$

and

$$D_{j,K} = (D_{j,K})_f(\theta)2^{-\alpha_r} \quad \ldots . \quad (34)$$

where α_r is the same exponent as that occurring in the expression for the specific reaction rate given in Eq. (25). Next we introduce the following dimensionless parameters :

$$\Lambda_{1,1} = \frac{\lambda_f(M_1)^{1-n_1}}{m^2\bar{c}_p}\left(\frac{p}{R_gT_f}\right)^{n_1}(\nu_{1,1}'' - \nu_{1,1}')B_1 \quad \ldots . \quad (35)$$

$$\beta_r = \frac{B_r}{B_1}\left(\frac{p}{R_gT_f}\right)^{n_r-n_1}(M_1)^{n_1-n_r} \quad \ldots . \quad (36)$$

and

$$\delta_{j,r} = \frac{M_j}{M_1}\frac{(\nu_{j,r}'' - \nu_{j,r}')}{(\nu_{1,1}'' - \nu_{1,1}')} \quad \ldots . \quad (37)$$

where $R_g = R/M_1$ and $\beta_1 = \delta_{1,1} = 1$. In view of Eqs. (33) to (37), Eq. (32) can be written in the following convenient form:

$$\frac{d\varepsilon_j}{d\theta} = \Lambda_{1,1}\frac{\sum_r[\beta_r\delta_{j,r}(\theta)^{1-n_r}\exp(-\theta_r/\theta)\prod_{l=1}^{s}(X_l)^{\nu_{l,r}'}]}{[(\theta - 1) + \sum_j(\varepsilon_j - \varepsilon_{j,f})(h_j^0/\bar{c}_pT_f)]} \quad \ldots . \quad (38)$$

As a simple illustration for the use of Eq. (38) we consider the one-step chemical reaction

$$N_2H_4 \rightarrow 2NH_2$$

In this case, as was noted in Section I*B*, it is found that

$$\sum_{j=1}^{s}(\varepsilon_j - \varepsilon_{j,f})\frac{h_j^0}{\bar{c}_pT_f} = (1 - \varepsilon_2)(1 - \theta_0)$$

if the subscript 2 identifies the species NH_2, the mole fraction of which increases from 0 to 1. Since $\beta_r = \beta_1 = 1$, $\delta_{j,r} = \delta_{1,1} = 1$ and $n_r = 1$, it is now seen that Eq. (38) reduces to the following simple expression

$$\frac{d\varepsilon_2}{d\theta} = -\Lambda_{1,1}\frac{X_1\exp(-\theta_1/\theta)}{(\theta - 1) + (1 - \varepsilon_2)(1 - \theta_0)}$$

or, since $\varepsilon_1 + \varepsilon_2 = X_1 + X_2 = 1$,

$$\frac{d\varepsilon_1}{d\theta} = \Lambda_{1,1}\frac{X_1\exp(-\theta_1/\theta)}{(\theta - 1) + (1 - \theta_0)\varepsilon_1} \quad \ldots . \quad (38a)$$

We now reduce Eq. (29) in a manner similar to that used in treating Eq. (28). Thus we choose the reference diffusion coefficient $D_{1,2}$ for diffusion of species 1 into species 2, and write

$$D_{j,K} = \frac{1}{\mu_{j,K}}D_{1,2} \quad \ldots . \quad (39)$$

Also, let

$$\varphi_j = M_1/M_j \quad \ldots . \quad (40)$$

Now all of the diffusion equations contain the dimensionless parameter

$$\lambda R_g T/\bar{c}_p p D_{1,2}$$

Introducing the temperature dependence for λ and $D_{1,2}$ through Eqs. (33) and (34) it is seen that the group

$$\alpha_1 = \frac{\lambda R_g T}{\bar{c}_p p D_{1,2}} = \frac{\lambda_f R_g T_f}{\bar{c}_p p (D_{1,2})_f} \qquad \ldots\ (41)$$

is independent of temperature. Equation (29) becomes now

$$\frac{dX_j}{d\theta} = \alpha_1 \frac{\sum_{K=1}^{s} \mu_{j,K} (X_j \varphi_K \varepsilon_K - X_K \varphi_j \varepsilon_j)}{[(\theta - 1) + \Sigma(\varepsilon_j - \varepsilon_{j,f})(h_j^0/\bar{c}_p T_f)]} \qquad \ldots\ (42)$$

As a simple illustration for the use of Eq. (42) we consider again the one-step chemical reaction

$$N_2H_4 \rightarrow 2NH_2$$

for which $\varphi_1 = 1$, $\varphi_2 = 2$ and $\mu_{1,2} = 1$. Hence Eq. (42) becomes simply

$$\frac{dX_2}{d\theta} = \alpha_1 \frac{X_2\varepsilon_1 - 2X_1\varepsilon_2}{[(\theta - 1) + (1 - \varepsilon_2)(1 - \theta_0)]}$$

$$\text{or} \quad \frac{dX_1}{d\theta} = \alpha_1 \frac{2X_1 - \varepsilon_1 - X_1\,\varepsilon_1}{[(\theta - 1) + (1 - \theta_0)\,\varepsilon_1]} \qquad \ldots\ (42a)$$

The mathematical problem of laminar flame propagation has now been reduced to the solution of the differential equations given in Eqs. (38) and (42), subject to the specified boundary conditions. The solution leads to different eigenvalues $\Lambda_{1,1}$ for different values of the diffusion parameter α_1. The mathematical dependence of $\Lambda_{1,1}$ on α_1 is difficult to obtain in general. However, as will be shown in the following sections, two important special cases permit simple analytical solutions. One special solution to the problem of laminar flame propagation is obtained in the extreme case where diffusion may be neglected completely. This is the viewpoint of the pure thermal theory. Without diffusion Eq. (42) is deleted and the boundary-value problem is reduced to the solution of Eq. (38), with the additional conditions $\varepsilon_j = Y_j$.

The second case, which is of practical interest since it corresponds roughly to ' best estimates ' for the diffusion coefficients, is that in which α_1 is of the order of unity. The nature of the solution for this special case is discussed more fully in the following section.

G. Some general results which can be obtained without complete solution of the eigenvalue problem

Useful conclusions can be obtained under fairly general conditions for the dependence of the mass flow m on pressure and on chemical reaction rate, as well as for the variation of X_1 with θ for $\alpha_1 = 1$. These results will now be described briefly.

(*a*) *Dependence of m on pressure*—For one-step chemical reactions the mass flow rate m is determined as a function of the parameters

$$A \equiv -A_{1,1} = -\frac{\lambda_f}{m^2 \bar{c}_p}\left(\frac{p}{R_g T_f}\right)^{n_1}(M_1)^{1-n_1}(\nu_{1,1}'' - \nu_{1,1}')B_1$$

$$\text{and} \quad \alpha_1 = \frac{\lambda_f R_g T_f}{\bar{c}_p p (D_{1,2})_f}$$

We note that α_1 is independent of pressure since $(D_{1,2})_f$ varies inversely as the pressure. Hence, for given values of A and α_1

$$m^2 = \frac{\lambda_f}{A\bar{c}_p}\left(\frac{p}{R_g T_f}\right)^{n_1}(M_1)^{1-n_1}(\nu_{1,1}' - \nu_{1,1}'')B_1$$

Introducing the laminar burning velocity u_0 through the relation

$$m = \rho_0 u_0$$

and using the equation of state

$$p = \rho_0 R_g T_0 = \rho R_g T M_1/\bar{M}$$

it follows that

$$u_0 \simeq (p)^{(n_1/2)-1} \qquad \ldots . \quad (43)$$

For a zero-, first- and second-order reaction, it is seen that u_0 varies, respectively, as $(p)^{-1}$, $(p)^{(-\frac{1}{2})}$ or is independent of pressure*.

The preceding conclusions hold also for simultaneous and interdependent chemical reactions if the reactions are all of the same order. If the reactions are of different orders, but a rate-controlling chemical reaction exists, then the pressure dependence of u_0 is determined, approximately, by the order of the rate-controlling reaction.

(*b*) *Relation between weight fraction and temperature for* $\alpha_1 = 1$—A simple and instructive relation can be found for the case of a one-step reaction if $\alpha_1 = 1$. We shall derive this relation for reactions of the type $A \rightarrow B$ for which the energy equation can be written in the form [*cf* Eq. (16*a*)] :

$$\frac{\lambda}{m\bar{c}_p}\frac{d\theta}{dx} = (\theta - 1) + \varepsilon_1(1 - \theta_0)$$

The diffusion equation has been given in Eq. (21) and for $M_1 = M_2$, $X_1 + X_2 = \varepsilon_1 + \varepsilon_2 = 1$, simply becomes

$$\frac{dX_1}{dx} = \frac{1}{D_{1,2}}\frac{m}{c_t M_1}[X_1(1 - \varepsilon_1) - (1 - X_1)\varepsilon_1]$$

For $\alpha_1 = 1$ it follows that

$$\frac{\lambda}{m\bar{c}_p} = \frac{\rho D_{1,2}}{m} = \frac{c_t M_1}{m} D_{1,2}$$

whence addition of $\dfrac{(1 - \theta_0)\rho D_{1,2}}{m}\dfrac{dX_1}{dx}$ to $\dfrac{\lambda}{m\bar{c}_p}\dfrac{d\theta}{dx}$ leads to the result

$$\frac{\lambda}{m\bar{c}_p}\left[\frac{d\theta}{dx} + (1 - \theta_0)\frac{dX_1}{dx}\right] = (\theta - 1) + X_1(1 - \theta_0) \quad \ldots \quad (44)$$

i.e.

$$X_1 = (1 - \theta)/(1 - \theta_0) \qquad \ldots . \quad (45)$$

is a particular solution of the differential equation which satisfies the

* For a number of hydrocarbon flames u_0 has been found to be independent of the pressure. This result shows that for these flames the rate-controlling or global reaction is of the second order.

boundary conditions provided X_1 decreases from 1 to 0 as θ increases from θ_0 to 1. Since for reactions of the type $A \rightarrow B$, $X_1 = Y_1$, it follows from Eq. (45) that

$$\bar{c}_p (T_f - T) = \bar{c}_p(T_f - T_0) Y_1$$

or $$\bar{c}_p T + \bar{c}_p(T_f - T_0) Y_1 + h_2^0 = \bar{c}_p T_f + h_2^0 = \text{constant}$$

But $\bar{c}_p(T_f - T_0) = h_1^0 - h_2^0$ and also $Y_1 + Y_2 = 1$. Therefore, it follows that

$$\bar{c}_p T + \bar{c}_p(T_f - T_0) Y_1 + h_2^0 = (\bar{c}_p T + h_1^0) Y_1 + (\bar{c}_p T + h_2^0) Y_2$$
$$= h_1 Y_1 + h_2 Y_2 = \text{constant}$$

Hence Eq. (45) leads to the conclusion that the sum of the thermal and chemical enthalpies remains constant during flow.

For the hydrazine decomposition flame treated in Section II and for the ozone decomposition flame treated in Section III, 'best estimates' of the diffusion coefficients[7] show that the effective values of α_1 are close to unity. Furthermore, for these two special cases, the mole fraction of the reactant decreases practically to zero. Therefore, for the solution of the relevant boundary value problems it is reasonable to postulate, by analogy with Eq. (45), that

$$\mathrm{d}X_1/\mathrm{d}\theta = \text{constant}$$

can be used as a first approximation in order to determine the eigenvalue $\Lambda_{1,1}$.

H. Summary remarks concerning the solution of problems presented in Sections II and III

The purpose of the discussions presented in Sections II and III is to obtain good approximate solutions to the flame equations by analytical methods. As illustrations have been chosen : (*a*) a one-step chemical reaction (*viz* the hydrazine decomposition flame), and (*b*) a chain reaction (*viz* the ozone decomposition flame). Our choice of examples was suggested by the fact that Hirschfelder and his collaborators[7] give a complete compilation of the required physicochemical parameters, which we adopt without criticism. In this manner we shall be able to compare our approximate solutions with the numerical calculations which have been carried out with great ambition and industry, and for which we are especially grateful to Professor Hirschfelder and his collaborators.

The fundamental idea of the mathematical method used to effect solution of the requisite eigenvalue problem is somewhat different for the thermal theory and for the complete theory with diffusion parameter α_1 of order unity, although in both cases integration is facilitated by separation of variables and by taking into account the properties of integrals of the form

$$\int_{\theta_i}^{1} \theta^{m'} \exp(-\theta_r/\theta)\mathrm{d}\theta$$

In the thermal theory the ε_j's are equal to the weight fractions Y_j. Thus the mole fractions X_j occurring in the reaction rate law can be expressed

arithmetically in terms of the ε_j's. Consequently a separation of variables is achieved when we approximate $\theta - 1$ in the expression

$$(\theta - 1) + \sum_{j=1}^{s} (\varepsilon_j - \varepsilon_{j,f})(h_j^0/\bar{c}_p T_f)$$

in terms of the ε_j's so that the right-hand side of Eq. (15) becomes a function of the ε_j's alone. The desired approximate expression for $1 - \theta$ in terms of the ε_j's is obtained from Eq. (38) by investigating the behaviour of $(1 - \theta)$ near the point $\theta \to 1$. The use of this technique has already been described for reactions of the type $A \to B$ and $nA \to n'B$[8, 14].

For problems in which the diffusion parameter α_1 is of order unity we do not have arithmetic relations between the mole fractions X_j and the parameters ε_j. However, the desired separation of variables may be achieved by assuming an approximation of the form

$$dX_j/d\theta = \text{constant}$$

which is suggested by the result obtained in Eq. (45) for the special case $A \to B$. The expression

$$(\theta - 1) + \sum_{j=1}^{s} (\varepsilon_j - \varepsilon_{j,f})(h_j^0/\bar{c}_p T_f)$$

is reduced as in the thermal theory.

The reader will recognize that ideas similar to ours appear in the papers of Semenov, Zeldovich, and Frank-Kamenetsky[4] and of Boys and Corner[5]. However, the Russian scientists disregard the convection term corresponding to $(1 - \theta)$ in their thermal theories ; their diffusion theories are practically restricted to reactions of the type $A \to B$. Boys and Corner[5] also neglect the convection term and replace $\exp(-\theta_r/\theta)$ by $\exp(-\theta_r)$ in first approximation. Then they improve on the first approximation by numerical iteration. We believe that the first approximation of Boys and Corner is rather crude because of the rapid change in value of the function $\exp(-\theta_r/\theta)$ even in the neighbourhood of $\theta = 1$.

II. THE HYDRAZINE DECOMPOSITION FLAME*

The thermal theory of one-dimensional, constant-pressure deflagration for the hydrazine decomposition flame has been discussed in a previous publication[14]. The assumed global reaction or rate-controlling process is[7]

$$N_2H_4 \to 2NH_2 \qquad \ldots . \quad (46)$$

We shall review briefly in Section II*A* the thermal theory of laminar flame propagation for the hydrazine decomposition flame. In Section II*B* this flame, with proper allowance for diffusion transport, is analyzed. Comparison of the calculated results with experimental data and with the results obtained by numerical calculations is carried out in Section II*C*.

A. Thermal theory[14]

In the absence of diffusion transport $V_j = 0$ and it follows from Eq. (6) that $\varepsilon_j = Y_j$. For the one-step chemical reaction described by Eq. (46) the

* At the suggestion of the senior author, Dr F. E. Marble has worked out an approximate analytical solution to the hydrazine decomposition flame with diffusion by representing X and θ as a two term series in $(1 - \varepsilon)$ and $(1 - \varepsilon)^2$. The mathematical procedure and the results obtained are similar to those described in the text.

basic differential equation has been given in Eq. (38*a*) *viz*

$$\frac{d\varepsilon_1}{d\theta} = \Lambda_{1,1}\frac{X_1 \exp(-\theta_1/\theta)}{[(\theta-1)+(1-\theta_0)\varepsilon_1]} = -\Lambda\frac{X_1 \exp(-\theta_1/\theta)}{[(\theta-1)+(1-\theta_0)\varepsilon_1]}$$

if $\Lambda = \Lambda_{1,1}(\nu_{1,1}'' - \nu_{1,1}') = -\Lambda_{1,1}$. But, according to Eq. (1)

$$X_1 = \frac{1-Y_2}{1+Y_2} = \frac{1-\varepsilon_2}{1+\varepsilon_2}$$

where the subscripts 1 and 2 identify the chemical species N_2H_4 and NH_2, respectively. Therefore the basic differential equation becomes

$$\Lambda\frac{1-\varepsilon_2}{1+\varepsilon_2}\exp(-\theta_1/\theta)\frac{d\theta}{d\varepsilon_2} = (\theta-1)+(1-\theta_0)(1-\varepsilon_2). \quad . \quad . \quad . \quad (47)$$

where, according to Eq. (35),

$$\Lambda = -\Lambda_{1,1} = \frac{\lambda_f p}{m^2 \bar{c}_p R_g T_f} B_1 \qquad R_g = R/M_1 \quad . \quad . \quad . \quad (48)$$

The boundary conditions are

$$\theta = \theta_i \text{ for } \varepsilon_2 = 0 \qquad \theta = 1 \text{ for } \varepsilon_2 = 1 \quad . \quad . \quad . \quad (49)$$

The solution of the boundary-value problem determined by Eqs. (47) to (49) leads to the desired eigenvalue for Λ. According to the method of VON KÁRMÁN and MILLÁN[8], two solutions for $\theta = \theta(\varepsilon_2)$ are found. One is a fair approximation for θ not very different from unity but ε_2 not necessarily small; the other solution is valid for very small values of ε_2, θ being arbitrary. The first solution is obtained by replacing the term $1-\theta$ on the right-hand side of Eq. (47) by an approximation of the form

$$1-\theta = (1/D)(1-\varepsilon_2) \quad . \quad . \quad . \quad (50)$$

where the constant D is determined by applying Eq. (47) to the singular point $\theta = 1$, $\varepsilon_2 = 1$. We obtain

$$D = \frac{1+(\Lambda/2)\exp(-\theta_1)}{1-\theta_0}$$

At this point it may be of interest to note that $1/D$ turns out to be a small number and that an error made in the estimate of the term $1-\theta$ has only a small effect on the final result. For the sake of clarity the resulting θ *versus* ε curve is summarized in *Fig. 1*.

The approximation introduced by Eq. (50) permits integration of Eq. (47) in the form

$$2\exp\theta_1\int_\theta^1 \exp(-\theta_1/\theta)d\theta = \frac{1-\theta_0}{1+(\Lambda/2)\exp(-\theta_1)}\int_{\varepsilon_2}^1 (1+\varepsilon_2)d\varepsilon_2 \quad . \quad . \quad . \quad . \quad (51)$$

On the other hand, for values of ε_2 small compared to unity, we obtain

$$\Lambda\int_{\theta_i}^{\theta}\frac{\exp(-\theta_1/\theta)}{\theta-\theta_0}d\theta = \varepsilon_2 \quad . \quad . \quad . \quad . \quad (52)$$

It is then assumed that the latter solution is valid for $\theta_i < \theta < \theta_t$ whereas Eq. (51) holds for $\theta_t < \theta < 1$. Here θ_t is a reduced transition temperature

which is determined by the condition that both θ and $d\theta/d\varepsilon_2$ are continuous at the point of transition. It turns out that the resulting value of Λ, for all reasonable ignition temperatures θ_i, is independent both of the value of the ignition temperature and of the value of the transition temperature.

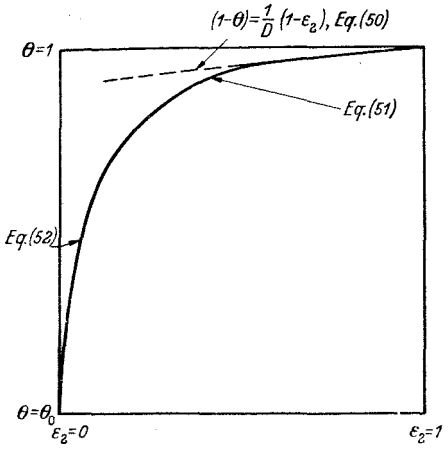

Fig. 1. Schematic representation of the dependence of $Y_2 = \varepsilon_2$ on θ for the thermal theory of laminar flame propagation supported by the decomposition of hydrazine

Therefore Λ can be determined in a simpler way by carrying out the integration in Eq. (51) between the limits $\theta = 0$ and $\theta = 1$, $\varepsilon_2 = 0$ and $\varepsilon_2 = 1$, respectively. Thus we have

$$2 \exp \theta_1 \int_0^1 \exp (-\theta_1/\theta) d\theta = \frac{1 - \theta_0}{1 + (\Lambda/2) \exp (-\theta_1)} \int_0^1 (1 + \varepsilon_2) d\varepsilon_2 \quad \ldots . \quad (53)$$

which leads to the relation

$$\Lambda = 2 \exp \theta_1 \left[\frac{\frac{3}{4}(1 - \theta_0)}{1 + \theta_1 \exp (\theta_1) E_i(-\theta_1)} - 1 \right] \quad \ldots . \quad (54)$$

where E_i represents the exponential integral defined by

$$-E_i(\theta_1) = \int_{\theta_1}^{\infty} (1/z) \exp (-z) dz$$

For $\theta_1 \gg 1$, Eq. (54) reduces to the expression

$$\Lambda \simeq 2 \exp \theta_1 [\tfrac{3}{4}\theta_1(1 - \theta_0)(1 + 2/\theta_1) - 1] \quad \ldots . \quad (54a)$$

The laminar burning velocity, u_0, is then obtained from Eq. (48) by replacing m by $\rho_0 u_0$. Introduction of the numerical[7] values used by Hirschfelder *et al* shows[14] that $u_0 = 300$ cm/sec for $B_1 = 4 \times 10^{12}$ sec^{-1}, $A_1 = 60{,}000$ cal/mole, $T_0 = 423$°K, $T_f = 1933$°K, $\bar{c}_p = 0{\cdot}6623$ cal/g. °K, and $\lambda_f = 6{\cdot}7 \times 10^{-3}$ cal/cm °K sec. It has been pointed out recently that a misprint occurs in the paper of Murray and Hall[15] and that the correct value of λ_f is $6{\cdot}7 \times 10^{-4}$ cal/cm °K sec. Hence the calculated value of u_0 is 95 cm/sec, which is in approximate agreement with the result $u_0 = 111$ cm/sec obtained by Murray and Hall from the flame theory of Zeldovich and Frank-Kamenetsky[4].

B. Hydrazine decomposition flame with diffusion

For the hydrazine decomposition flame with diffusion transport the basic differential equations have been given in Eqs. (38*a*) and (42*a*) and are repeated here for the sake of convenience :

$$\frac{d\varepsilon_1}{d\theta} = -\Lambda \frac{X_1 \exp(-\theta_1/\theta)}{(\theta - 1) + (1 - \theta_0)\varepsilon_1} \quad \ldots\ (55)$$

$$\frac{dX_1}{d\theta} = \alpha_1 \frac{2X_1 - \varepsilon_1 - X_1\varepsilon_1}{(\theta - 1) + (1 - \theta_0)\varepsilon_1} \quad \ldots\ (56)$$

Here Λ has been given in Eq. (48) and, according to Eq. (41),

$$\alpha_1 = \frac{R_g \lambda_f T_f}{p(D_{1,2})_f \bar{c}_p} = \frac{R_g \lambda T}{p D_{1,2} \bar{c}_p} \quad \ldots\ (57)$$

The parameter α_1 characterizes the ratio between heat conduction and diffusion coefficients.

In order to establish an efficient method of approximation we consider the process in the light of the general results given in Section I*G*. Evidently both X_1 and ε_1 decrease from unity at the cold boundary ($\theta = \theta_0$) to zero at the hot boundary ($\theta = 1$). According to Eq. (55), the eigenvalue Λ is determined by the expression

$$\int_1^0 [(\theta - 1) + (1 - \theta_0)\varepsilon_1] d\varepsilon_1 = -\Lambda \int_0^1 X_1 \exp(-\theta_1/\theta) d\theta \ldots . (58)$$

It has been shown in Section I*G* that for reactions of the type $A \rightarrow B$ and for $\alpha_1 = 1$ the relation

$$X_1(1 - \theta_0) = (1 - \theta)$$

holds, which corresponds to the broken straight line of *Fig. 2*. We believe that the true behaviour of $X_1(\theta)$ for variable molecular weight and for values of α_1 of the order of unity will correspond to a curve like the solid curve shown in *Fig. 2*. Because of the rapid decrease of the factor

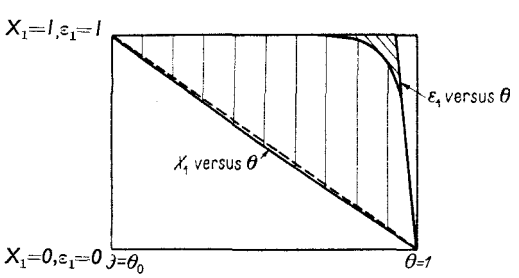

Fig. 2. Schematic representation of the θ versus ε_1 *and* θ versus X_1 *curves for the hydrazine decomposition flame, based on a complete theory of laminar flame propagation*

$\exp(-\theta_1/\theta)$, only the portion of the function $X_1(\theta)$ for small values of $(1 - \theta)$ makes an appreciable contribution to the value of the integral appearing on the right-hand side of Eq. (58). Therefore a linear functional form

$$X_1 = C(1 - \theta) \quad \ldots\ (59)$$

will serve as a fair approximation.

Consider now the integral appearing on the left-hand side of Eq. (58). Since the bulk of the chemical reactions occurs at temperatures close to the

adiabatic flame temperature, the parameter ε_1 increases with $1 - \theta$ more rapidly than X_1 and will approach the line $\varepsilon_1 = 1$ asymptotically as shown schematically in *Fig. 2*. As a matter of fact, the entire integral is represented graphically by the area of *Fig. 2* which is shaded vertically. It is seen that the contribution of the term $\theta - 1$ is relatively small compared to the contribution of $\varepsilon_1(1 - \theta_0)$. Furthermore, if we replace $1 - \theta$ by the approximation

$$(1 - \theta) = (1/D')\varepsilon_1 \qquad \ldots . \quad (60)$$

the resulting error in the estimate of the integral is given by the small densely shaded area of *Fig. 2*.

On the basis of the preceding arguments it appears that it is only necessary to determine the numerical factors C and D' from the behaviour of X_1 and ε_1 at the singular point $\theta \to 1$. We take into account the fact that $D' \gg C$ and obtain first approximations from Eqs. (55) and (56) :

$$C = \frac{\alpha_1}{1 - \theta_0} \qquad D' = \frac{[A\alpha_1 \exp(-\theta_1)]^{\frac{1}{2}}}{1 - \theta_0} \qquad \ldots . \quad (61)$$

Since it is well known that A is larger for flames with diffusion than for flames without diffusion, a lower limit for $A \exp(-\theta_1)$ is 31, which corresponds to the result obtained from a thermal theory of flame propagation[14]. Hence it is clear by reference to Eq. (61) that D' is, in fact, at least five times as large as C.

Introduction of Eqs. (59) and (60) into Eq. (58) leads to the following result in view of the relations given for C and D' in Eq. (61) :

$$(1 - \theta_0)\int_0^1 \varepsilon_1 \left[1 - \frac{1}{\{A\alpha_1 \exp(-\theta_1)\}^{\frac{1}{2}}}\right] d\varepsilon_1 = \frac{A\alpha_1}{1-\theta_0}\int_0^1 (1 - \theta)\exp(-\theta_1/\theta)d\theta \qquad \ldots . \quad (62)$$

The integral appearing on the right-hand side of Eq. (62) is equal to $[\exp(-\theta_1)]/(\theta_1)^2$ multiplied by a function $g(\theta_1)$, where $g(\theta_1)$ is given, in good approximation, by the following semi-convergent series:

$$g(\theta_1) = 1 - \frac{6}{\theta_1} + \frac{36}{(\theta_1)^2} - \frac{240}{(\theta_1)^3} + \frac{1800}{(\theta_1)^4} \qquad \ldots . \quad (63)$$

Let us first neglect the second term in the bracket appearing on the left-hand side of Eq. (62). Then we obtain the following zero'th order approximation:

$$A = \frac{\exp\theta_1}{2\alpha_1}\frac{(1 - \theta_0)^2}{g(\theta_1)}(\theta_1)^2 \qquad \ldots . \quad (64)$$

Introduction of appropriate numerical values[7] on the right-hand side of Eq. (64) shows again that $A\alpha_1 \exp(-\theta_1)$ is large compared to unity. If the expression for A given in Eq. (64) is substituted on the left-hand side of Eq. (62), a useful first approximation results for A *viz*

$$A = \frac{\exp\theta_1}{2\alpha_1}\frac{(1 - \theta_0)^2}{g(\theta_1)}\left[1 - \frac{\{2\,g(\theta_1)\}^{\frac{1}{2}}}{(1 - \theta_0)\theta_1}\right](\theta_1)^2 \qquad \ldots . \quad (65)$$

It is a relatively simple matter to improve the preceding analysis by solving Eqs. (55) and (56) for C and D' more exactly. The resulting expression for A yields, however, only a slight correction to the value of A obtained from Eq. (65).

The values of Λ for $\theta_1 = 15{\cdot}62$, $\theta_0 = 0{\cdot}219$ and $\alpha_1 = 2/(3 \times 0{\cdot}75) = 0{\cdot}889$ or $\alpha_1 = 2/(3 \times 1{\cdot}5) = 0{\cdot}444$ obtained from Eq. (65), are contrasted in *Table 1* with the corresponding results derived by numerical solution of the differential equations and presented by Hirschfelder *et al*[7]. Reference to the data listed in *Table 1* shows excellent agreement between the numerical values, thereby suggesting that Eq. (65) represents an adequate approximation to the solution of the differential equations describing laminar flame propagation supported by the decomposition of hydrazine.

Table 1. Comparison of values of Λ calculated from Eq. (65) with the results of numerical calculations given in reference 7

α_1	$\Lambda \times 10^{-8}$	
	From Eq. (65)	*From reference 7*
0·889	6·27	6·00
0·444	12·5	11·2

The linear burning velocity u_0 is obtained from Eq. (48) by setting $m = \rho_0 u_0$. Thus

$$u_0 = \theta_0 \left(\frac{B_1 \lambda_f R_g T_f}{p \bar{c}_p \Lambda} \right)^{\frac{1}{2}} \quad \ldots . \quad (66)$$

or, using Eq. (65) for Λ,

$$u_0 = \frac{1}{(1 - \theta_0)\theta_1} \frac{\lambda_f}{\rho_0 \bar{c}_p} \left[\frac{2B_1 \exp(-\theta_1)}{(D_{1,2})_f} \right]^{\frac{1}{2}} \left[\frac{g(\theta_1)}{1 - \{2g(\theta_1)\}^{\frac{1}{2}}/(1 - \theta_0)\theta_1} \right]^{\frac{1}{2}} \quad \ldots . \quad (67)$$

Reference to Eq. (67) shows the interesting result that, even including the effects of diffusion, u_0 is proportional to the square root of the specific reaction rate at T_f. This result is of considerable importance in connection with the concept of ' global chemical reactions ' for complex combustion processes.

C. Comparison of calculated and measured burning velocities for the hydrazine decomposition flame

The laminar burning velocities calculated from Eq. (67) are given in *Table 2* together with the data from reference 7 and the result calculated on the basis

Table 2. Laminar burning velocities u_0 for the hydrazine decomposition flame : $N_2H_4 \rightarrow 2NH_2$

u_0 (*cm/sec*) *obtained from :*	*For*		
	$\alpha_1 = 0{\cdot}889$	$\alpha_1 = 0{\cdot}444$	*Thermal theory*
Reference 7, based on numerical calculations	40·2	31·6	—
Eq. (67)	39·3	27·9	—
Reference 14, based on a thermal theory ..	—	—	95

of a thermal theory[14].* Reference to the data listed in *Table 2* shows excellent agreement between the calculated values.

* The numerical data obtained by HIRSCHFELDER *et al* have been divided by 3·16 in order to correct for the revision of λ_f from $6{\cdot}7 \times 10^{-3}$ cal/cm. °K sec. to $6{\cdot}7 \times 10^{-4}$ cal/cm. °K sec.

The experimental value for the laminar burning velocity, as given by Murray and Hall[15], is 200 cm/sec. Therefore, the calculated values of u_0 are much too low and, furthermore, allowance for diffusion transport increases the discrepancy between theory and experiment for the hydrazine decomposition flame.

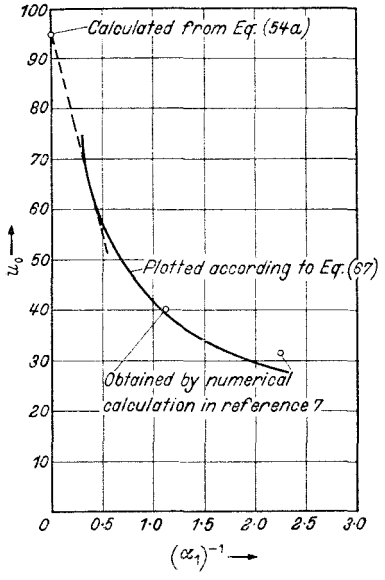

Fig. 3. Laminar burning velocity for the hydrazine decomposition flame as a function of $(\alpha_1)^{-1}$*; for the thermal theory (zero diffusion coefficient)* $(\alpha_1)^{-1} = 0$

We may summarize the results of the present section with the remark that our simple approximate formulae replace, with very good success, the cumbersome numerical calculations of Hirschfelder and his collaborators. On the other hand, it is also apparent that the physicochemical processes occurring in the flame are not adequately described by the one-step decomposition of hydrazine and the diffusion of NH_2 into the reactant gases, at least not if the kinetics data proposed by Murray and Hall[15] are valid.

III. THE OZONE DECOMPOSITION FLAME

It is the purpose of the present discussion to extend the techniques described in Section II to the solution of the flame equations describing one-dimensional, constant-pressure deflagration supported by the decomposition of ozone in a combustible mixture consisting of oxygen and ozone.

In Section III*A* a complete formulation of the problem is presented, using the kinetic scheme applied by Hirschfelder and his collaborators[7]. However, the composition of the gas mixture is described by using the two predominant chemical species, O_2 and O_3, as independent variables, whereas Hirschfelder *et al* chose O and O_3.

An important simplification of the general equations is obtained in Section III*B* by comparing the magnitudes of the various chemical reaction rates. The thermal theory of the ozone decomposition is developed in Section III*C* and an upper limit is obtained for the laminar burning velocity. A first approximation to u_0 according to a complete theory is obtained in Section III*D*, where assumptions similar to those introduced in the study of the hydrazine decomposition flame are used to effect solution of the flame equations.

A. Basic equations

In this section a summary of the relevant basic equations as derived from Eqs. (38) and (42) is presented.

The complete kinetic scheme for the ozone decomposition flame is assumed to be the following[7] :

$$O_3 + G \xrightarrow{k_1} O + O_2 + G \qquad \ldots\ (68)$$

$$O + O_2 + G \xrightarrow{k_2} O_3 + G \qquad \ldots\ (69)$$

$$O + O_3 \xrightarrow{k_3} 2O_2 \qquad \ldots\ (70)$$

$$2O_2 \xrightarrow{k_4} O + O_3 \qquad \ldots\ (71)$$

$$O_2 + G \xrightarrow{k_5} 2O + G \qquad \ldots\ (72)$$

$$2O + G \xrightarrow{k_6} O_2 + G \qquad \ldots\ (73)$$

The symbol G in Eqs. (68), (69), (72) and (73) means that chemical changes can occur only as the result of a collision between the reactants undergoing chemical change (and specified explicitly in the equations) with one particle of any of the species O, O_2 or O_3. The atom or molecule G does not undergo chemical change as the result of the reaction. The presence of G increases the order of the reaction by unity ; the mole fraction X_G has the value one. The specific reaction rate constants k_1 to k_6 are defined by Eqs. (68) to (73), respectively, and correspond to the symbols k_1, k_1', k_2, k_2', k_3 and k_3' of Hirschfelder *et al*[7].

The complete expressions for $d\varepsilon_j/d\theta$ are given by Eq. (38) and can be written out explicitly without difficulty. The parameters β_1 to β_6 correspond to Eqs. (68) to (73), respectively, with β for Eq. (68) chosen as reference parameter. It is then clear that

$$\beta_1 = 1 \qquad \beta_2 = \frac{B_2}{B_1}\left(\frac{p}{RT_f}\right)$$

$$\beta_3 = \frac{B_3}{B_1} \qquad \beta_4 = \frac{B_4}{B_1} \qquad \beta_5 = \frac{B_5}{B_1}$$

$$\beta_6 = \frac{B_6}{B_1}\left(\frac{p}{RT_f}\right)$$

Also if $j = 1, 2, 3$, correspond to O, O_2 and O_3, respectively,

$$\delta_{1,1} = 1 \qquad \delta_{2,1} = 2 \qquad \delta_{3,1} = -3$$
$$\delta_{2,2} = -2 \qquad \delta_{3,2} = 3 \qquad \delta_{2,3} = 4 \qquad \delta_{3,3} = -3$$
$$\delta_{2,4} = -4 \qquad \delta_{3,4} = 3 \qquad \delta_{2,5} = -2$$
$$\delta_{3,5} = 0 \qquad \delta_{2,6} = 2 \qquad \delta_{3,6} = 0$$

Appropriate numerical values for B_1 to B_6 and β_1 to β_6, based on the data of reference 7, are summarized in *Table 3*.

In terms of β_1 to β_6, and using the known numerical values of the $\delta_{i,j}$, it is found that Eq. (38) leads to the following result :

$$\frac{d\varepsilon_2}{d\theta} = \frac{A_{1,1}}{[(\theta - 1) + \sum_j (\varepsilon_j - \varepsilon_{j,f})(h_j^0/\bar{c}_p T_f)]} \left[\frac{2}{\theta} \exp(-\theta_1/\theta) X_3 \right.$$
$$- \frac{2}{\theta^2} \beta_2 \exp(-\theta_2/\theta) X_1 X_2 + \frac{4}{\theta} \beta_3 \exp(-\theta_3/\theta) X_1 X_3$$
$$- \frac{4}{\theta} \beta_4 \exp(-\theta_4/\theta)(X_2)^2 - \frac{2}{\theta} \beta_5 \exp(-\theta_5/\theta) X_2$$
$$\left. + \frac{2}{\theta^2} \beta_6 \exp(-\theta_6/\theta)(X_1)^2 \right]$$

or

$$\frac{d\varepsilon_2}{d\theta} = \frac{(2/\theta) A_{1,1}(X_3) \exp(-\theta_1/\theta)}{[(\theta - 1) + \Sigma(\varepsilon_j - \varepsilon_{j,f})(h_j^0/\bar{c}_p T_f)]} \left[1 - \frac{\beta_2}{\theta} \exp(-\Delta\theta_2/\theta) \left(\frac{X_1 X_2}{X_3}\right) \right.$$
$$+ 2\beta_3 \exp(-\Delta\theta_3/\theta)(X_1) - 2\beta_4 \exp(-\Delta\theta_4/\theta) \frac{(X_2)^2}{X_3}$$
$$\left. - \beta_5 \exp(-\Delta\theta_5/\theta) \left(\frac{X_2}{X_3}\right) + \frac{\beta_6}{\theta} \exp(-\Delta\theta_6/\theta) \frac{(X_1)^2}{X_3} \right] \quad . \quad . \quad . \quad (74)$$

Table 3. Numerical values for some of the physicochemical parameters occurring in the ozone decomposition flame, computed from the data given in reference 7 ($\alpha_f = 1/2$)

Parameter	*Numerical value**	*Parameter*	*Numerical value*	*Parameter*	*Numerical value*	*Parameter*	*Numerical value*
$B_1 \times 10^{-12}/\sqrt{T_f}$	10·56	β_1	1·000	θ_1	9·719	—	—
$B_2 \times 10^{-12}/\sqrt{T_f}$	0·230	β_2	$1{\cdot}743 \times 10^{-7}$	θ_2	0	$\Delta\theta_2$	− 9·719
$B_3 \times 10^{-12}/\sqrt{T_f}$	7·15	β_3	0·6771	θ_3	2·416	$\Delta\theta_3$	− 7·303
$B_4 \times 10^{-12}/\sqrt{T_f}$	2·93	β_4	0·2775	θ_4	39·94	$\Delta\theta_4$	30·22
$B_5 \times 10^{-12}/\sqrt{T_f}$	8·92	β_5	0·8447	θ_5	47·24	$\Delta\theta_5$	37·52
$B_6 \times 10^{-12}/\sqrt{T_f}$	0·482	β_6	$3{\cdot}653 \times 10^{-7}$	θ_6	0	$\Delta\theta_6$	− 9·719

* The dimensions of the values listed in the second column are those of the appropriate frequency factor multiplied by temperature raised to the negative one half power.

Similarly,

$$\frac{d\varepsilon_3}{d\theta} = \frac{A_{1,1}}{[(\theta - 1) + \sum_j (\varepsilon_j - \varepsilon_{j,f})(h_j^0/\bar{c}_p T_f)]} \left[-\frac{3}{\theta} \exp(-\theta_1/\theta)(X_3) + \frac{3}{\theta^2} \beta_2 \exp(-\theta_2/\theta)(X_1 X_2) - \frac{3}{\theta} \beta_3 \exp(-\theta_3/\theta)(X_1 X_3) + \frac{3}{\theta} \beta_4 \exp(-\theta_4/\theta)(X_2)^2 \right]$$

or

$$\frac{d\varepsilon_3}{d\theta} = \frac{-(3/\theta) A_{1,1}(X_3) \exp(-\theta_1/\theta)}{[(\theta - 1) + \sum_j (\varepsilon_j - \varepsilon_{j,f})(h_j^0/\bar{c}_p T_f)]} \left[1 - \frac{\beta_2}{\theta} \exp(-\Delta\theta_2/\theta) \left(\frac{X_1 X_2}{X_3} \right) + \beta_3 \exp(-\Delta\theta_3/\theta)(X_1) - \beta_4 \exp(-\Delta\theta_4/\theta) \frac{(X_2)^2}{X_3} \right] \quad \ldots (75)$$

Here

$$\left. \begin{array}{l} \Delta\theta_2 = \theta_2 - \theta_1, \quad \Delta\theta_3 = \theta_3 - \theta_1, \\ \Delta\theta_4 = \theta_4 - \theta_1, \quad \Delta\theta_5 = \theta_5 - \theta_1, \\ \Delta\theta_6 = \theta_6 - \theta_1 \end{array} \right\} \quad \ldots . (76)$$

Appropriate numerical values for θ_1 to θ_6 and $\Delta\theta_1$ to $\Delta\theta_6$, computed from the data of reference 7, are also summarized in *Table 3*.

Explicit diffusion equations are obtained from Eq. (42). We note that the molecular weight ratios have the following numerical values

$$\varphi_1 = 1, \ \varphi_2 = \tfrac{1}{2}, \ \varphi_3 = \tfrac{1}{3}$$

We follow Hirschfelder in estimating the ratios of the binary diffusion coefficients. According to Hirschfelder *et al*[7], the parameters $\mu_{j,K}$ introduced by Eq. (39) can be obtained from the following relation :

$$\mu_{j,K} = \frac{D_{1,2}}{D_{j,K}} = \frac{M_j M_K}{M_j + M_K} \frac{M_1 + M_2}{M_1 M_2} = \frac{3}{32} \frac{M_j M_K}{M_j + M_K} \quad \ldots . (39a)$$

The preceding expression is derived from the kinetic theory of gases for rigid elastic spheres using estimates for the collision cross sections which appear to be doubtful. Fortunately, it will be found that the calculated burning velocity is a weak function of the assumed relation between the binary diffusion coefficients. The coefficients $\mu_{j,K}$ calculated from Eq. (39*a*) are

$$\mu_{2,1} = \mu_{1,2} = 1, \ \mu_{3,2} = \mu_{2,3} = \tfrac{9}{5} \text{ and } \mu_{3,1} = \mu_{1,3} = \tfrac{9}{8}$$

Hence Eq. (42) leads to the relations

$$\frac{dX_2}{d\theta} = \frac{\alpha_1}{[(\theta - 1) + \Sigma(\varepsilon_j - \varepsilon_{j,f})(h_j^0/\bar{c}_p T_f)]} (\varepsilon_1 X_2 - \tfrac{1}{2}\varepsilon_2 X_1 + \tfrac{3}{5}\varepsilon_3 X_2 - \tfrac{9}{10}\varepsilon_2 X_3) \quad \ldots . (77)$$

and

$$\frac{dX_3}{d\theta} = \frac{\alpha_1}{[(\theta - 1) + \Sigma(\varepsilon_j - \varepsilon_{j,f})(h_j^0/\bar{c}_p T_f)]} (\tfrac{9}{8} X_3 \varepsilon_1 - \tfrac{3}{8} X_1 \varepsilon_3 + \tfrac{9}{10} X_3 \varepsilon_2 - \tfrac{3}{5} X_2 \varepsilon_3) \quad \ldots . (78)$$

It is clear from the definition for $\bar{c}_p$ given in Eq. (11) that the denominator of Eq. (78) vanishes at $\theta = 1$. For the present purposes it will be sufficient to obtain an approximate expression for the term

$$(\theta - 1) + \sum_{j=1}^{s} (\varepsilon_j - \varepsilon_{j,f}) \frac{h_j^0}{\bar{c}_p T_f}$$

by noting that $h_2^0 = 0$, $\varepsilon_{1,f} \simeq 0$, $\varepsilon_{1,0} \simeq 0$, $\varepsilon_{3,f} \simeq 0$. Therefore

$$(\theta - 1) + \sum_{j=1}^{s} (\varepsilon_j - \varepsilon_{j,f}) \frac{h_j^0}{\bar{c}_p T_f} = (\theta - 1) + a_1\varepsilon_1 + a_3\varepsilon_3 \quad \ldots . \quad (79)$$

where $$a_1 = h_1^0/\bar{c}_p T_f \qquad a_3 = h_3^0/\bar{c}_p T_f \quad \ldots . \quad (80)$$

and $\bar{c}_p$ is obtained from Eq. (11), which becomes explicitly

$$\bar{c}_p = \frac{\varepsilon_{3,0}\, h_3^0}{T_f - T_0} \quad \ldots . \quad (81)$$

i.e. $a_3 = \dfrac{1}{\varepsilon_{3,0}}(1 - \theta_0)$.

The general flame equations for the ozone decomposition flame can now be written in convenient form by combining Eqs. (74), (75), (77) and (78) with Eq. (79). The results are*

$$\frac{d\varepsilon_2}{d\theta} = \frac{(2/\theta)A_{1,1}(X_3)\exp(-\theta_1/\theta)}{(\theta-1) + a_1\varepsilon_1 + a_3\varepsilon_3}\left[1 - (\beta_2/\theta)\left(\frac{X_1X_2}{X_3}\right)\exp(-\Delta\theta_2/\theta) + 2\beta_3(X_1)\exp(-\Delta\theta_3/\theta) - 2\beta_4\frac{(X_2)^2}{X_3}\exp(-\Delta\theta_4/\theta) - \beta_5\left(\frac{X_2}{X_3}\right)\exp(-\Delta\theta_5/\theta) + \frac{\beta_6}{\theta}\frac{(X_1)^2}{X_3}\exp(-\Delta\theta_6/\theta)\right] \quad \ldots . \quad (82)$$

$$\frac{d\varepsilon_3}{d\theta} = \frac{(-3/\theta)A_{1,1}(X_3)\exp(-\theta_1/\theta)}{(\theta-1) + a_1\varepsilon_1 + a_3\varepsilon_3}\left[1 - (\beta_2/\theta)\left(\frac{X_1X_2}{X_3}\right)\exp(-\Delta\theta_2/\theta) + \beta_3(X_1)\exp(-\Delta\theta_3/\theta) - \beta_4\frac{(X_2)^2}{X_3}\exp(-\Delta\theta_4/\theta)\right] \quad \ldots . \quad (83)$$

$$\frac{dX_2}{d\theta} = \frac{\alpha_1(\varepsilon_1X_2 - \frac{1}{2}\varepsilon_2X_1 + \frac{3}{5}\varepsilon_3X_2 - \frac{9}{10}\varepsilon_2X_3)}{(\theta - 1) + a_1\varepsilon_1 + a_3\varepsilon_3} \quad \ldots . \quad (84)$$

$$\frac{dX_3}{d\theta} = \frac{\alpha_1(\frac{9}{8}\varepsilon_1X_3 - \frac{3}{8}\varepsilon_3X_1 + \frac{9}{10}\varepsilon_2X_3 - \frac{3}{5}\varepsilon_3X_2)}{(\theta - 1) + a_1\varepsilon_1 + a_3\varepsilon_3} \quad \ldots . \quad (85)$$

We have now deduced a set of four simultaneous differential equations [*cf* Eqs. (82) to (85)] for the four unknowns ε_2, ε_3, X_2 and X_3. All of these equations are non-linear. Without essential simplification the equations can be solved only by investing a tremendous effort in numerical calculations. The solution is a major operation even with the use of the best electronic computing machines. Fortunately, a closer analysis of the interdependence between the individual reactions and comparison of the orders of magnitude of the different reaction rates leads to a very significant simplification of the mathematical problem. This method of approach has two obvious advantages: (*1*) the methods of solution described in the preceding section can be

* In terms of the parameter a used in reference 7 for the ozone decomposition flame, it is readily shown that

$$A_{1,1} = \frac{10{\cdot}56}{Tf}\frac{a}{m^2}$$

Similarly, the parameter δ of reference 7 is related to α_1 through the expression $\alpha_1 = 4/3\delta$.

utilized almost without modification; (*2*) by introducing an assumption analogous to the steady-state approximation for chain carriers in classical chemical kinetics, we arrive at a better understanding of the physical problem. The ' extended steady-state ' hypothesis may well prove to be useful for the solution of a wide variety of flow problems with chain reactions.

B. Simplification of the eigenvalue problem

An acceptable theoretical picture for the ozone decomposition flame must describe the disappearance and production of ozone in the flame. Later in this section a complete calculation will be presented, comparing orders of magnitude for the reaction rates corresponding to all of the processes occurring in the ozone decomposition flame. However, in order to amplify our ideas, it is advantageous if the discussion is introduced with some preliminary qualitative remarks.

Ozone is removed by the reactions

(*1*) $$O_3 + G \rightarrow O + O_2 + G$$

(*3*) $$O + O_3 \rightarrow 2O_2$$

It is produced by the reactions

(*2*) $$O + O_2 + G \rightarrow O_3 + G$$

(*4*) $$2O_2 \rightarrow O + O_3$$

The quantity of ozone produced by the process (*2*), which is the reverse of reaction (*1*), would be expected to be negligible compared to that removed by reaction (*1*), except possibly at very low temperatures or under conditions in which the oxygen atom concentration is of the same order of magnitude as, or greater than, the ozone concentration. Reaction (*4*), the bimolecular reaction between oxygen molecules to form O and O_3, has an extremely high activation energy (*cf* the value of θ_4 in *Table 3*) and therefore will not be important except at very high temperatures. Similarly, the reaction

(*5*) $$O_2 + G \rightarrow 2O + G$$

can be important only at extremely high temperatures since the activation energy for this process is even larger than for reaction (*4*) (compare the values of θ_5 and θ_4 given in *Table 3*). Finally, the inverse process

(*6*) $$2O + G \rightarrow O_2 + G$$

can play a vital part only for unreasonably large values of the oxygen atom concentration.

Thus it appears that the important reactions are (*1*) and (*3*), both of which consume O_3, whereas (*1*) produces and (*3*) removes O. There are two conditions under which (*1*) and (*3*) would not furnish an acceptable, approximate description of the chemistry in the ozone decomposition flame :

(*a*) when the mole fraction of the chain carrier, X_1, is not very small

(*b*) when the mole fraction X_1 is small but of the same order of magnitude as, or larger than, X_3.

The case (*b*) must arise as the combustion reactions go to completion since the mole ratio of O to O_3 at thermodynamic equilibrium is known to be appreciably larger than unity. Reference to the numerical solutions

obtained by Hirschfelder *et al*[7] shows, in fact, that very elaborate calculations are required to describe the concentration profiles in a temperature range extending from a few degrees below the adiabatic flame temperature to T_f. As thermodynamic equilibrium is approached, reaction (*3*) must become unimportant whereas reaction (*2*) plays a dominant role so that the oxygen atom concentration is practically determined by the equilibrium between reactions (*1*) and (*2*) *i.e.* in this temperature range

$$(X_1)/(X_3) \simeq 5{\cdot}74 \times 10^6 \times (\theta) \times \exp(-9{\cdot}719/\theta)$$

The ratio X_1/X_3 approaches a value of 345 as θ approaches unity*.

On the basis of the preceding considerations we now introduce the following basic hypothesis : throughout the entire flame, except in a very close temperature interval in the region between T_f' and T_f, the mole fraction X_1 is small compared to X_3. Hence also $X_1 \ll X_2$. Therefore, as has been said before, the two reactions (*1*) and (*3*) determine the production and consumption of the oxygen atoms. Furthermore, since the rate constant of (*3*) is much larger than that of (*1*), it is reasonable to assume that oxygen atoms are consumed by (*3*) practically as rapidly as they are produced by (*1*). If we consider only reactions (*1*) and (*3*) then it follows that

$$X_1 = (B_1/B_3) \exp(\Delta\theta_3/\theta) = 1{\cdot}48 \exp(-7{\cdot}30/\theta) \quad \ldots \quad (86)$$

The mole fraction X_1 has been computed as a function of temperature according to Eq. (86). The results of these calculations are plotted in *Fig. 4*.

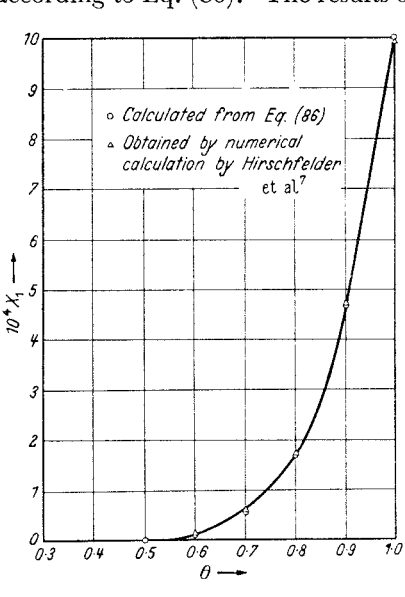

Fig. 4. Mole fraction of oxygen atoms, X_1, as a function of the reduced temperature θ for the ozone decomposition flame

It is seen that X_1 approaches the value 1×10^{-3} as θ approaches unity. Also plotted in *Fig. 4* are the values of X_1 as a function of θ obtained by numerical solution of the flame equations[7].

Reference to *Fig. 4* shows very excellent agreement between our approximate estimates for X_1 and the values of X_1 obtained by Hirschfelder *et al*[7].

* Hirschfelder *et al* give the equilibrium value X_1/X_3 as 283 corresponding to a pressure of 1 atm rather than to 0·821 atm, which was used in the experimental studies. The calculated values of u_0 are quite insensitive to the pressure.

up to temperatures which are very close to the adiabatic flame temperature. The approximation on which our calculation is based can be expressed also in the form $d\varepsilon_1/d\theta = 0$. At first sight the statement $d\varepsilon_1/d\theta = 0$ appears to be contradictory to the fact that ε_1 is a function of θ and, therefore, cannot vanish exactly. However, setting $d\varepsilon_1/d\theta$ equal to zero means only that, in first approximation, ε_1 is a slowly varying function of the temperature compared to ε_2 and ε_3. The close agreement between our calculated X_1 *versus* θ curve and that obtained by Hirschfelder *et al* shows that the influence of the chemical reactions which we have neglected is not large.

Our conclusions do not apply to the temperature range in which the mole fraction of oxygen atoms drops from about 10^{-3} to the equilibrium value 10^{-8} at the adiabatic flame temperature. The decrease in oxygen atom concentration is probably caused primarily by reaction (*2*), the influence of which is no longer negligible as soon as the concentration of O_3 is equal to, or less than, the concentration of O. We see no convincing arguments to justify the assumption $d\varepsilon_1/d\theta = 0$ in this temperature 'boundary range', except for the equilibrium condition itself. We believe, however, that the processes in the boundary range have little or no influence on the combustion velocity. The last remark is apparently justified not only by the satisfactory agreement with the burning velocity obtained by numerical calculations but also by the good agreement with experiment (compare Sections III*C* and III*D*). Therefore, it appears that for the purpose of calculating the laminar burning velocity only a small error is made if we equate T_f' to T_f as is done in the calculations described below.

On the basis of our calculations and of the work of Hirschfelder *et al*[7], we must conclude that the picture underlying some of the 'diffusion theories' of laminar flame propagation is untenable. Thus it appears that the build-up of the concentration of the free radicals is not caused by diffusion from the hot boundary into partially burnt gas and that the maximum concentration of chain carriers is not determined by the equilibrium conditions at T_f. We may summarize the physical meaning of our results by noting that (*a*) the build-up of oxygen atoms is caused primarily by a competition between the reactions producing and consuming oxygen atoms, and (*b*) the maximum concentration of oxygen atoms existing at temperatures close to T_f is about five orders of magnitude larger than the equilibrium value.

We shall now justify in greater detail our neglect of all but reactions (*1*) and (*3*) and we shall show that the net result of these two processes is removal of O_3 at double the rate corresponding to process (*1*) alone.

The remarks made above are summarized by the statements

$$\left.\begin{aligned} &\varepsilon_2 + \varepsilon_3 = 1 \\ &X_1/X_3 \ll 1 \\ &d\varepsilon_2/d\theta = -\,d\varepsilon_3/d\theta \end{aligned}\right\} \qquad \ldots\ (87)$$

The relation $d\varepsilon_2/d\theta = -\,d\varepsilon_3/d\theta$ can be used together with Eqs. (82) and (83) to obtain the following result :

$$\begin{aligned} -1 + (2\beta_6/\theta)(X_1^2/X_3)\exp(-\Delta\theta_6/\theta) + (\beta_2/\theta)(X_1X_2/X_3)\exp(-\Delta\theta_2/\theta) \\ = -\beta_3(X_1)\exp(-\Delta\theta_3/\theta) + \beta_4(X_2^2/X_3)[\exp(-\Delta\theta_4/\theta)] \\ [1 + (2\beta_5/\beta_4)(1/X_2)\{\exp-(\Delta\theta_5 - \Delta\theta_4)/\theta\}] \qquad \ldots\ (88) \end{aligned}$$

But the numerical values given in *Table 3* show that

$$(2\beta_5/\beta_4)(1/X_2)[\exp - (\Delta\theta_5 - \Delta\theta_4)/\theta] = (6{\cdot}09/X_2) \exp (- 7{\cdot}30/\theta)$$

where $X_2 \sim 1$ and $0 \leqslant \theta \leqslant 1$; hence this term can always be neglected in comparison with unity. Similarly,

$$(2\beta_6/\theta)(X_1)(X_1/X_3) \exp (-\Delta\theta_6/\theta) = (7{\cdot}31 \times 10^{-7}/\theta)(X_1)(X_1/X_3)[\exp (9{\cdot}72/\theta)]$$

will always be negligibly small compared to unity, for all reasonable values of X_1, if $X_1/X_3 < 1$. For example, for θ equal to 0·9 and $X_1/X_3 < 1$ we obtain

$$\frac{2\beta_6}{\theta} \exp (- \Delta\theta_6/\theta)(X_1) \left(\frac{X_1}{X_3}\right) < 4 \times 10^{-5}$$

Furthermore, the term

$$\frac{\beta_2}{\theta} \exp (- \Delta\theta_2/\theta)(X_2) \left(\frac{X_1}{X_3}\right) = \frac{1{\cdot}743 \times 10^{-7}}{\theta} \exp (9{\cdot}72/\theta)(X_2) \left(\frac{X_1}{X_3}\right)$$

can be neglected relative to unity if X_1/X_3 is appreciably less than unity. Finally, the term

$$\beta_4 \exp (- \Delta\theta_4/\theta)(X_2) \left(\frac{X_2}{X_3}\right) < 0{\cdot}278 \exp (- 30{\cdot}22/\theta) \left(\frac{X_2}{X_3}\right)$$

is negligibly small compared to unity unless X_2/X_3 is greater even than the equilibrium ratio at T_f. Hence Eq. (88) becomes, approximately,

$$\beta_3 \exp (- \Delta\theta_3/\theta)(X_1) = 1$$

and Eqs. (82) and (83) reduce to the following simple expression :

$$\frac{d\varepsilon_3}{d\theta} = - \frac{d\varepsilon_2}{d\theta} = - 6\Lambda_{1,1} \frac{(X_3/\theta) \exp (- \theta_1/\theta)}{(\theta - 1) + a_3\varepsilon_3} \quad \ldots . \quad (89)$$

In order to complete the formulation of the eigenvalue problem, subject to the approximations given in Eq. (87), we now note that the expression for diffusion of O_3, given in Eq. (85), becomes

$$\frac{dX_3}{d\theta} = \alpha_1 \frac{\frac{9}{10} X_3 - \frac{3}{5}\varepsilon_3 - \frac{3}{10} X_3\varepsilon_3}{(\theta - 1) + a_3\varepsilon_3} \quad \ldots . \quad (90)$$

In the following paragraphs the simplified relations given in Eqs. (89) and (90) will be solved by utilizing the same methods as were employed in Section II for the study of the hydrazine decomposition flame.

C. The thermal theory of laminar flame propagation supported by the decomposition of ozone for $\varepsilon_{3,0} = 1/3$

The thermal theory of laminar flame propagation will yield an upper limit for the linear burning velocity. For a thermal theory it is evident that $V_3 = 0$ and, from Eq. (7), $\varepsilon_3 = Y_3 =$ weight fraction of ozone. Also, in general,

$$X_3 = (\overline{M}/M_3) Y_3$$

For $\varepsilon_{3,0} = 1/3$ it follows that $\overline{M}$ varies from an initial value of 36 to a final value of 32. Hence we may equate $\overline{M}$ to 34 and $\overline{M}/M_3$ to 17/24 without introducing an appreciable error.

In the absence of diffusion the flame equations reduce, therefore, to the single expression

$$\frac{d\Upsilon_3}{d\theta} = -\frac{17}{4}\frac{\Lambda_{1,1}}{\theta}\exp(-\theta_1/\theta)\frac{\Upsilon_3}{(\theta-1)+a_3\Upsilon_3} \quad \ldots\ (91)$$

We proceed to determine $\Lambda_{1,1}$ from Eq. (91) by a straightforward application of the Kármán–Millán technique[8]. Thus

$$\lim_{\theta\to 1}\frac{d\Upsilon_3}{d\theta} = -\frac{1}{a_3}\left(\tfrac{17}{4}\Lambda_{1,1}\exp(-\theta_1)+1\right) \quad \ldots\ (92)$$

From Eqs. (91) and (92) for $\theta \simeq 1$ it follows that

$$\frac{\Upsilon_3}{(\theta-1)+a_3\Upsilon_3} = \frac{1+\tfrac{17}{4}\Lambda_{1,1}\exp(-\theta_1)}{\tfrac{17}{4}\Lambda_{1,1}\exp(-\theta_1)a_3} \quad \ldots\ (93)$$

Introducing Eq. (93) on the right-hand side of Eq. (91) leads to the result

$$\frac{d\Upsilon_3}{d\theta} = -\frac{1+\tfrac{17}{4}\Lambda_{1,1}\exp(-\theta_1)}{a_3\exp(-\theta_1)}\frac{1}{\theta}\exp(-\theta_1/\theta)$$

Integration of the preceding relation between $\Upsilon_3 = \frac{1}{3}$, $\theta = 0$ and $\Upsilon_3 = 0$, $\theta = 1$ leads to the result

$$\Lambda_{1,1}\exp(-\theta_1) \simeq \tfrac{4}{51}\left[\frac{a_3\theta_1}{\left\{1-\frac{1}{\theta_1}+\frac{2}{(\theta_1)^2}-\frac{6}{(\theta_1)^3}+\frac{24}{(\theta_1)^4}\right\}}-3\right] \quad \ldots\ (94)$$

For $a_3 = 2{\cdot}28$ and $\theta_1 = 9{\cdot}72$ it is seen that $\Lambda_{1,1}\exp(-\theta_1) = 1{\cdot}67$ or, in the notation of Hirschfelder *et al*[7],

$$\frac{a}{m^2} = \frac{T_f}{10{\cdot}56}\Lambda_{1,1} = 3{\cdot}29\times 10^6$$

This result is seen to be in excellent agreement with the value $a/m^2 = 3{\cdot}2\times 10^6$ obtained by numerical calculations[7].

The laminar burning velocity is obtained from $\Lambda_{1,1}\exp(-\theta_1) = 1{\cdot}67$ by using Eq. (35) in the form

$$u_0 = \frac{M_1}{\overline{M}_0}\theta_0\left(\frac{1}{\Lambda_{1,1}}\frac{\lambda_f B_1}{M_1\bar{c}_p}\right)^{\frac{1}{2}}$$

where $\overline{M}_0 = \frac{9}{4}M_1$ is the initial molecular weight of the gas mixture. The resulting value of u_0 for $\lambda_f = 1{\cdot}860\times 10^{-4}$ cal/cm °K sec, $T_0 = 300$°K and $T_f = 1250$°K is found to be $u_0 = 84$ cm/sec.

D. The ozone decomposition flame with diffusion

It has been shown that introduction of the approximations $\varepsilon_2 + \varepsilon_3 = 1$ and $X_1/X_3 \ll 1$ reduces the set of equations describing the ozone decomposition flame to Eqs. (89) and (90) *viz*

$$\frac{d\varepsilon_3}{d\theta} = -6\Lambda_{1,1}\frac{(X_3/\theta)\exp(-\theta_1/\theta)}{(\theta-1)+a_3\varepsilon_3}$$

and

$$\frac{dX_3}{d\theta} = \alpha_1\frac{\frac{9}{10}X_3 - \frac{3}{5}\varepsilon_3 - \frac{3}{10}X_3\,\varepsilon_3}{(\theta-1)+a_3\varepsilon_3}$$

We shall now attempt to estimate the eigenvalue $\Lambda_{1,1}$ from these equations by introducing approximations analogous to those used in the case of the hydrazine decomposition flame with diffusion, viz.,

$$X_3 = \Psi_3(1 - \theta) \quad \ldots\ (95)$$

and

$$\varepsilon_3 = \eta_3(1 - \theta) \quad \ldots\ (96)$$

which have been justified, approximately, by the discussion given in Section I*G*(*b*) at least for the special case $\alpha_1 = 1$, $A \rightarrow B$.

We now write Eq. (89) in the form

$$\varepsilon_3 d\varepsilon_3 = - \frac{X_3}{a_3 - (1 - \theta)/\varepsilon_3} \frac{6\Lambda_{1,1}}{\theta} \exp(-\theta_1/\theta) d\theta$$

On the right-hand side of the preceding expression X_3 and ε_3 may be replaced, as a first approximation, according to Eqs. (95) and (96), respectively. If it is assumed that the resulting expression holds over the entire integration interval from θ_i to 1 and that θ_i is appreciably larger than θ_0 and appreciably smaller than 1, then it follows that, approximately,

$$-\tfrac{1}{6} \int_{\varepsilon_{3,0}}^{0} \varepsilon_3 d\varepsilon_3 = \frac{\Psi_3 \Lambda_{1,1}}{a_3 - (1/\eta_3)} \int_0^1 \frac{(1 - \theta) \exp(-\theta_1/\theta)}{\theta} d\theta$$

and

$$\frac{1}{\eta_3} = a_3 - \frac{12}{(\varepsilon_{3,0})^2} \Psi_3 \frac{\Lambda_{1,1} g'(\theta_1) \exp(-\theta_1)}{(\theta_1)^2} \quad \ldots\ (97)$$

where $g'(\theta_1)$ is given, approximately, by the following semi-convergent series :

$$g'(\theta_1) = 1 - \frac{4}{\theta_1} + \frac{18}{(\theta_1)^2} - \frac{96}{(\theta_1)^3} + \frac{600}{(\theta_1)^4} - \frac{4320}{(\theta_1)^5} + \cdots \quad \ldots\ (98)$$

By using Eqs. (95) and (96), Eqs. (89) and (90) become, respectively, for $\theta \simeq 1$:

$$\eta_3 = 6\Lambda_{1,1} \exp(-\theta_1) \frac{\Psi_3}{a_3\eta_3 - 1} \quad \ldots\ (99)$$

and

$$-\Psi_3 = \alpha_1 \frac{\frac{9}{10}\Psi_3 - \frac{3}{5}\eta_3}{a_3\eta_3 - 1} \quad \ldots\ (100)$$

Dividing Eq. (99) by Eq. (100) leads to the result

$$-\frac{\eta_3}{\Psi_3} = \frac{6\Lambda_{1,1} \exp(-\theta_1)}{\alpha_1} \frac{\Psi_3}{\frac{9}{10}\Psi_3 - \frac{3}{5}\eta_3}$$

or

$$\left(\frac{\eta_3}{\Psi_3}\right)^2 - \frac{3}{2}\left(\frac{\eta_3}{\Psi_3}\right) - \frac{10\Lambda_{1,1}}{\alpha_1} \exp(-\theta_1) = 0$$

Since η_3/Ψ_3 must be positive the only acceptable root of the preceding quadratic equation is given by the relation

$$\frac{\eta_3}{\Psi_3} = \tfrac{3}{4} + (\tfrac{9}{16} + \xi)^{\frac{1}{2}} \quad \ldots\ (101)$$

where

$$\xi = \frac{10\Lambda_{1,1}}{\alpha_1} \exp(-\theta_1) \quad \ldots\ (102)$$

We next combine Eqs. (100) and (101) and obtain the result

$$\Psi_3 = \frac{1 - \alpha_1\left[\frac{9}{10} - \frac{3}{5}\left\{\frac{3}{4} + \left(\frac{9}{16} + \xi\right)^{\frac{1}{2}}\right\}\right]}{a_3\left[\frac{3}{4} + \left(\frac{9}{16} + \xi\right)^{\frac{1}{2}}\right]}$$

or

$$\frac{1}{\eta_3} = \frac{a_3}{1 - \alpha_1\left[\frac{9}{10} - \frac{3}{5}\left\{\frac{3}{4} + \left(\frac{9}{16} + \xi\right)^{\frac{1}{2}}\right\}\right]} \quad \ldots\ldots (103)$$

From the explicit expression for Ψ_3 and Eq. (97) it follows that

$$\frac{1}{\eta_3} = a_3 - \frac{12}{(\varepsilon_{3,0})^2}\frac{A_{1,1}\exp(-\theta_1)}{(\theta_1)^2}g'(\theta_1)\frac{1 - \alpha_1\left[\frac{9}{10} - \frac{3}{5}\left\{\frac{3}{4} + \left(\frac{9}{16} + \xi\right)^{\frac{1}{2}}\right\}\right]}{a_3\left[\frac{3}{4} + \left(\frac{9}{16} + \xi\right)^{\frac{1}{2}}\right]}$$

or, in view of Eq. (102),

$$\frac{1}{\eta_3} = a_3 - \frac{1{\cdot}2}{(\varepsilon_{3,0})^2}\frac{\varepsilon_1\xi}{(\theta_1)^2}g'(\theta_1)\frac{1 - \alpha_1\left[\frac{9}{10} - \frac{3}{5}\left\{\frac{3}{4} + \left(\frac{9}{16} + \xi\right)^{\frac{1}{2}}\right\}\right]}{a_3\left[\frac{3}{4} + \left(\frac{9}{16} + \xi\right)^{\frac{1}{2}}\right]} \quad \ldots (104)$$

The two relations for $1/\eta_3$ given in Eqs. (103) and (104) determine ξ, and hence $A_{1,1}$ or u_0, as a function of the parameters which specify the problem *viz* $\varepsilon_{3,0}$, θ_0, θ_1 and α_1. The solution can be obtained graphically without difficulty. However, as we shall show presently, a good approximate solution can be obtained for some cases which are of practical importance by noting that for these $\xi \gg \frac{9}{16}$ and that $1 - 9\alpha_1/20$ may be neglected relative to $\frac{3}{5}\alpha_1\left(\frac{9}{16} + \xi\right)^{\frac{1}{2}} \simeq \frac{3}{5}\alpha_1\xi^{\frac{1}{2}}$; also $\frac{3}{4} + \left(\frac{9}{16} + \xi\right)^{\frac{1}{2}} \simeq \xi^{\frac{1}{2}}$. Introduction of these approximations into Eqs. (103) and (104) leads to the result

$$\frac{a_3}{\frac{3}{5}\alpha_1\xi^{\frac{1}{2}}} = a_3 - \frac{0{\cdot}72\alpha_1{}^2\xi g'(\theta_1)}{(\varepsilon_{3,0})^2 a_3(\theta_1)^2}$$

or, for sufficiently large values of ξ,

$$\xi \simeq \frac{a_3(\theta_1)^2(\varepsilon_{3,0})^2}{0{\cdot}72\alpha_1{}^2 g'(\theta_1)}\left[a_3 - \frac{1{\cdot}414\{g'(\theta_1)\}^{\frac{1}{2}}}{\theta_1(\varepsilon_{3,0})}\right]$$

But, according to Eqs. (80) and (81), $a_3 = \frac{1}{\varepsilon_{3,0}}(1 - \theta_0)$. Therefore the following, approximate, explicit relation is obtained for ξ:

$$\xi \simeq \frac{(1 - \theta_0)(\theta_1)^2}{0{\cdot}72\,\alpha_1{}^2 g'(\theta_1)}\left[(1 - \theta_0) - \frac{1{\cdot}414\{g'(\theta_1)\}^{\frac{1}{2}}}{\theta_1}\right] \quad \ldots (105)$$

i.e. for large values of ξ, ξ is independent of $\varepsilon_{3,0}$ and varies inversely as the square of α_1.

From Eqs. (35), (102) and (105) we can now obtain an explicit expression for u_0 subject to the limitation that ξ is large. Equations (35) and (102) are readily seen to lead to the result

$$u_0 = \frac{M_1}{\overline{M}_0}\theta_0\left[\frac{10\exp(-\theta_1)\lambda_f B_1}{\alpha_1\xi M_1\bar{c}_p}\right]^{\frac{1}{2}} \quad \ldots\ldots (106)$$

or, in view of Eq. (105),

$$u_0 = \frac{M_1\,\theta_0}{\overline{M}_0\,\theta_1}\left[\frac{7{\cdot}2\,\alpha_1 g'(\theta_1)\exp(-\theta_1)\lambda_f B_1}{(1 - \theta_0)\{(1 - \theta_0) - 1{\cdot}414\sqrt{g'(\theta_1)/\theta_1}\}M_1\bar{c}_p}\right]^{\frac{1}{2}}$$

Furthermore, according to Eq. (81), $\bar{c}_p = \varepsilon_{3,0}h_3^0/(T_f - T_0)$ whence, finally,

$$u_0 = \frac{M_1}{\overline{M}_0}\frac{\theta_0}{\theta_1}\left[\frac{7{\cdot}2\alpha_1 T_f g'(\theta_1)\exp(-\theta_1)\lambda_f B_1}{\{(1 - \theta_0) - 1{\cdot}414\sqrt{g'(\theta_1)/\theta_1}\}\varepsilon_{3,0}Mh_3^0}\right]^{\frac{1}{2}} \quad \ldots (107)$$

Reference to Eq. (107) shows that u_0 varies as the square root of α_1 just as for the hydrazine decomposition flame [compare Eq. (67)]; the initial composition of the gas mixture enters explicitly through $\varepsilon_{3,0}$ and $\overline{M}_0$; the initial gas temperature and the adiabatic flame temperature occur in the terms θ_0, θ_1, T_f, $g'(\theta_1)$, $\exp(-\theta_1)$. It should be noted that in our formulation the product $\lambda_f B_1$ is proportional to T_f since $B_1/\sqrt{T_f}$ is a constant (*cf* the footnote on p. 11) and $\lambda_f/\sqrt{T_f}$ is also a constant if $\alpha_r = \frac{1}{2}$ in Eq. (33). Therefore the following general expression is obtained for the ratio of burning velocities for two different gas mixtures

$$\frac{u_0}{u_0^*} = \frac{\overline{M}_0^*}{\overline{M}_0}\frac{T_0}{T_0^*}\frac{T_f}{T_f^*}\left[\left\{\frac{g'(\theta_1)}{g'(\theta_1^*)}\right\}\exp-(\theta_1-\theta_1^*)\times\left\{\frac{\varepsilon_{3,0}^*}{\varepsilon_{3,0}}\right\}\left\{\frac{1-\theta_0^*-1{\cdot}414\sqrt{g'(\theta_1^*)/\theta_1^*}}{1-\theta_0-1{\cdot}414\sqrt{g'(\theta_1)/\theta_1}}\right\}\right]^{\frac{1}{2}} \quad \ldots\ (108)$$

for fixed values of α_1, M_1 and h_3^0.

(*a*) *Laminar burning velocity for* $T_0 = 300°K$, $T_f = 1250°K$, $\varepsilon_{3,0} = \frac{1}{3}$, $\theta_1 = 9{\cdot}72$.—For $T_0 = 300°\mathrm{K}$, $T_f = 1250°\mathrm{K}$, $\theta_1 = 9{\cdot}72$ and $\varepsilon_{3,0} = \frac{1}{3}$, it is easily seen that Eqs. (103) and (104) become, respectively,

$$\frac{1}{\eta_3} = \frac{2{\cdot}28}{1-\alpha_1\left[\frac{9}{10}-\frac{3}{5}\left\{\frac{3}{4}+\left(\frac{9}{16}+\xi\right)^{\frac{1}{2}}\right\}\right]} \quad \ldots\ (103a)$$

and

$$\frac{1}{\eta_3} = 2{\cdot}28 - \frac{3{\cdot}47\times10^{-2}\alpha_1\xi\left[1-\alpha_1\left\{\frac{9}{10}-\frac{3}{5}\left[\frac{3}{4}+\left(\frac{9}{16}+\xi\right)^{\frac{1}{2}}\right]\right\}\right]}{\left[\frac{3}{4}+\left(\frac{9}{16}+\xi\right)^{\frac{1}{2}}\right]} \quad \ldots\ (104a)$$

The quantity $1/\eta_3$ is plotted as a function of ξ in *Fig. 5* for $\alpha_1 = 1{\cdot}42$ and $\alpha_1 = 1{\cdot}78$ according to Eqs. (103*a*) and (104*a*), respectively. Reference to the data plotted in *Fig. 5* leads to the numerical values summarized in *Table 4*. Also listed in *Table 4* are the results obtained by Hirschfelder *et al*

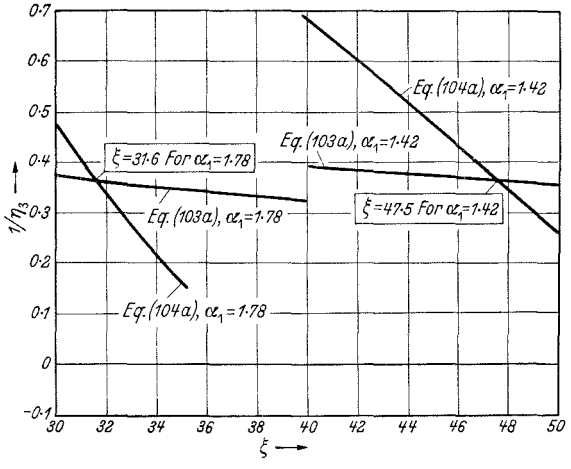

Fig. 5. Determination of the eigenvalues ξ *from Eqs. (103a) and (104a) for the ozone decomposition flame for two different values of the diffusion parameter* α_1

by means of numerical calculations[7]. Comparison between the data listed in *Table 4* shows satisfactory agreement between the calculated values. In

particular, it is evident that Eqs. (103*a*) and 104*a*) give, approximately, the dependence of $\Lambda_{1,1}$ on the parameter α_1. Thus for $\alpha_1 = 1{\cdot}78$ and $1{\cdot}42$ we obtain a ratio for the values of $\Lambda_{1,1}$ equal to $1{\cdot}22$ whereas the numerical calculations lead to the ratio $1{\cdot}17$. Our estimates for $\Lambda_{1,1}$ are larger than those of Hirschfelder *et al* by roughly 20 per cent, whence it follows that our calculated laminar burning velocities are smaller by roughly 10 per cent

Table 4. The quantities $\Lambda_{1,1}$ and Hirschfelder's parameter a/m^2 (for the ozone decomposition flame) for $\alpha_1 = 1{\cdot}42$ and $1{\cdot}78$

ξ *from Fig. 5 for*		$\Lambda_{1,1}=(\alpha_1/10)\xi \exp \theta_1$ *for*		$a/m^2 = (T_f/10{\cdot}56)\Lambda_{1,1}$ *for*		a/m^2 *from Hirschfelder for*	
$\alpha_1=1{\cdot}42$	$\alpha_1=1{\cdot}78$	$\alpha_1=1{\cdot}42$	$\alpha_1=1{\cdot}78$	$\alpha_1=1{\cdot}42$	$\alpha_1=1{\cdot}78$	$\alpha_1=1{\cdot}42$	$\alpha_1=1{\cdot}78$
47·5	31·6	$1{\cdot}12 \times 10^5$	$9{\cdot}36 \times 10^4$	$1{\cdot}38 \times 10^7$	$1{\cdot}11 \times 10^7$	$1{\cdot}04 \times 10^7$	$8{\cdot}9 \times 10^6$

[compare also Section III*D*(*b*)]. We attribute this small discrepancy primarily to the fact that the parameter α_1 differs appreciably from unity in the present calculations and that, therefore, the representations for X_3 and ε_3 given in Eqs. (95) and (96) fail to hold exactly.

Reference to *Fig. 5* shows that for the present calculations ξ is between 30 and 40. Hence we can utilize also the approximate explicit relation for ξ which is given in Eq. (105). For the specified values of T_0, T_f and $\varepsilon_{3,0}$, Eq. (105) becomes

$$\xi = 92{\cdot}2/\alpha_1^2 \qquad \ldots . \quad (107a)$$

which can easily be seen to lead to eigenvalues ξ that do not differ greatly from the values obtained graphically. The linear burning velocity is given by Eq. (106) or, to an adequate approximation, by Eq. (107) where $\overline{M}_0 = (9/4)M_1$ for $\varepsilon_{3,0} = 1/3$ and $\varepsilon_{2,0} = 2/3$.

The eigenvalues u_0 obtained by solving the pair of relations given in Eqs. (103*a*) and (104*a*) for $\alpha_1 = 1{\cdot}42$ and $1{\cdot}78$ are listed in *Table 5*. The

Table 5. Linear burning velocities for the ozone decomposition flame for a mixture containing initially 75 per cent of O_2 and 25 per cent of O_3 by volume

u_0 (*cm/sec*) *for thermal theory from*		u_0 (*cm/sec*) *for* $\alpha_1 = 1{\cdot}42$ *from*		u_0 (*cm/sec*) *for* $\alpha_1 = 1{\cdot}78$ *from*		u_0 (*cm/sec*) *experimental value from reference 17*
Eq. (106)	*Hirschfelder* et al[7]	*Eq. (106)*	*Hirschfelder* et al[7]	*Eq. (106)*	*Hirschfelder* et al[7]	
84	85	42	47	46	51	55

values of u_0 given by Eq. (107) are plotted as a function of α_1 in *Fig. 6*. Also shown in *Table 5* and in *Fig. 6* are the results obtained by numerical solution of the flame equations[7], the value determined in the preceding section from the thermal theory, and the experimental point estimated by LEWIS and VON ELBE from constant-volume experiments[16,17].

(*b*) *Comparison of calculated burning velocities and burning velocity ratios with the experimental data obtained by Lewis and von Elbe for different values of* $\varepsilon_{3,0}$, T_0 *and pressure*—The preceding calculations, and particularly the comparison with the results obtained by Hirschfelder *et al*, show that our simple methods for obtaining approximate analytical solutions are useful. Lewis and von Elbe[16] have published experimental measurements of the laminar burning velocity obtained in closed vessel experiments for ozone decomposition flames at different ratios of ozone to oxygen concentration and at different pressures.

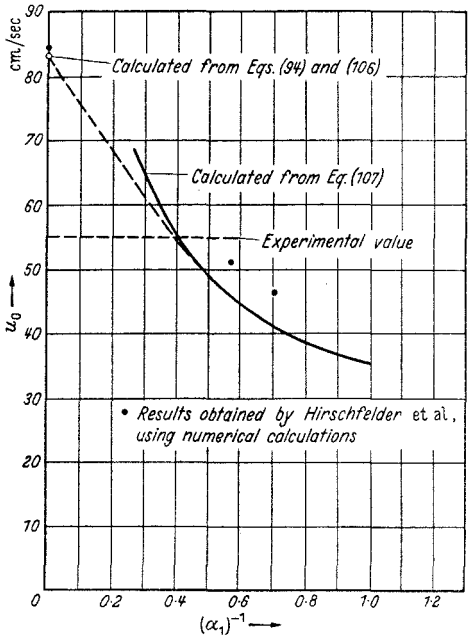

Fig. 6. Comparison between calculated and observed burning velocities for the ozone decomposition flame ($\varepsilon_{3,0}=\frac{1}{3}$, $T_0=300°K$, $T_f=1250°K$) *for different values of the diffusion parameter* $(\alpha_1)^{-1}$

We shall examine these experimental results and show that the observed trends are in approximate agreement with our theoretical calculations. This analysis is of particular interest because our formulae show no direct influence of pressure on u_0. Comparison with experimental data obtained at different pressures therefore affords a severe test for the validity of the formulation of the problem of laminar flame propagation supported by ozone decomposition.

We have listed in *Table 6* the results of representative burning velocity measurements published by Lewis and von Elbe[16,17]. It is clear from these results that ξ is sufficiently large to justify the use of Eq. (107) for approximate analysis. Thus although $\Lambda_{1,1}$ decreases for the faster burning compositions, this effect is partly compensated for, because ξ increases as the factor $\exp(-\theta_1)$ increases for the hotter combustible mixtures. The results of calculations based on Eq. (107) are also listed in *Table 6*. Not included in *Table 6* are measured laminar burning velocities obtained by Lewis and von Elbe towards the end of combustion in constant-volume experiments. For these high-pressure experiments the calculated values of u_0 agree roughly with the observed data. However, in view of some uncertainty in the

interpretation of the experimental measurement, we have not reproduced the relevant data in *Table 6*.

Reference to the data given in *Table 6* shows: (*a*) that our theoretical calculations predict, approximately, the observed trends for the change of u_0 with composition and pressure, although the theoretical relations give only an implicit dependence for u_0 on p through T_f; (*b*) our theoretical formula is clearly superior to that of Lewis and von Elbe[16], whose calculated

*Table 6. Comparison of linear burning velocities calculated from Eq. (107) with the values given by Lewis and von Elbe[16,17]**

$\varepsilon_{f,o}$	p mm Hg	T_o °K	T_f °K	u_o (cm/sec) determined experimentally	u_o (cm/sec) calculated from Eq. (107)	u_o (cm/sec) calculated by Lewis and von Elbe[16]
0·33	624	300	1239	55	41	253
0·50	367	301	1680	141	147	—
0·60	495	302	1922	160	225	333

burning velocities are also shown in *Table 6*. Unfortunately no comparison with Hirschfelder's work is possible since the laborious numerical calculations required for the preparation of *Table 6* have not yet been published by this author. However, we are confident that if and when these results become available they will not differ greatly from ours.

IV. CONCLUDING REMARKS

In conclusion we restate the principal results obtained in the present investigations. These are:

(*1*) Numerical solution of the flame equations can be obviated by making reasonable approximations. The results obtained, particularly for small or moderate burning velocities (*i.e.* for large values of the parameter $\Lambda_{1,1}$) are in excellent agreement with the data deduced by laborious numerical calculations.

(*2*) The influence of diffusion coefficients on laminar burning velocity has been expressed explicitly by utilizing approximations which are valid for the case $\alpha_1 \simeq 1$. Furthermore, useful analytical results have been obtained for thermal theories.

(*3*) It has been shown that the burning process can be described, approximately, by the rule that the total (chemical plus thermodynamic) enthalpy is constant. This statement is correct for the case $\alpha_1 \simeq 1$ for reactions of the type $A \rightarrow B$. It appears also that the assumption of a constant-enthalpy process is a useful concept, as a first approximation, for more general types of chemical reactions.

* In order to assure consistency in the calculations, the data for T_0 and Tf given by Lewis and von Elbe were used ; for $\varepsilon_{f,o} = 0{\cdot}50$ and $0{\cdot}60$, the integral

$$\int_0^1 \left(\frac{1-\theta}{\theta}\right) \exp\left(-\theta_1/\theta\right) \mathrm{d}\vartheta$$

was evaluated accurately because the semi-convergent approximation for $g'(\theta_1)$ does not yield a satisfactory result.

(*4*) It has been shown that a promising method for the computation of laminar burning velocities in systems with chain reactions involves an extension of the steady-state approximation for the concentration of chain carriers which is made in classical chemical kinetics. It appears that the use of this concept gives the correct order of magnitude for the build-up of free radicals, at least for the ozone decomposition flame. Our steady-state postulate is in contradiction to the hypothesis of Lewis and von Elbe[16] that equilibrium exists with respect to a particular chemical reaction. This equilibrium hypothesis leads to incorrect results, both as regards the concentration of free radicals and as regards the burning velocity, at least for the range of values of T_0 and p listed in *Table 6*. Hirschfelder's computations for the build-up of chain carriers are practically the same as ours, except that he includes in his calculations chemical reactions the influence of which has been shown to be negligibly small. However, his argument that 'the concentration of free radicals near the hot boundary is greatly in excess of thermal equilibrium' because 'the oxygen atoms are essentially in equilibrium in the region of the hot boundary' is different from our interpretation of the results based on an extended steady-state approximation.

The authors believe that a straightforward application of the extended steady-state hypothesis to chain reactions will be useful for the solution of a wide variety of flow problems with chemical reactions, provided no excessively large temperature gradients occur. Specifically, a study of the hydrogen–bromine flame and of hydrocarbon flames in general may prove to be useful. In this connection we wish to restate the physical concept on which our hypothesis is based : The concentration of chain carriers changes with temperature. However, as long as appreciable concentrations of reactants remain, the rate of change of concentration of chain carriers with temperature is small compared to the rate of change of concentration of reactants with temperature. The extended steady-state approximation must fail to apply as the combustion reactions go to completion ; however, the processes occurring during the terminal stage of combustion exert only a minor influence on the laminar burning velocity.

FRENCH SUMMARY

On présente le système complet des équations de la théorie de la flamme laminaire, où l'on tient compte à la fois de la conduction de la chaleur et de la diffusion, avec un nombre arbitraire de réactions simultanées. On pose également le problème de valeur propre déterminant la vitesse de propagation de la flamme. On donne deux exemples montrant qu'il est possible d'obtenir des expressions analytiques approchées de la célérité de la flamme qui sont en bon accord avec les résultats de l'intégration numérique des équations. Dans le premier exemple (décomposition de l'hydrazine) une des réactions est considérée comme globalement déterminante. Dans le second exemple (décomposition de l'ozone) on introduit sur la concentration des radicaux libres O *une hypothèse correspondant à l'approximation d'état stationnaire utilisée généralement en cinétique chimique. Dans les deux cas, les célérités mesurées se placent entre les valeurs fournies par les théories sans et avec diffusion, le coefficient étant, dans ce dernier*

cas, celui déterminé par le Professeur Hirschfelder à partir des données de la théorie cinétique des gaz.

Les formules explicites sont obtenues avec une approximation raisonnable et sans hypothèses trop limitatives : celle faite notamment dans l'étude de la flamme de décomposition de l'ozone permettrait sans doute aussi de mieux comprendre le mécanisme des réactions en chaîne en général. La méthode indiquée dans cet exposé laisse espérer que les réactions en chaîne les plus compliquées, telles que la combustion des hydrocarbures, pourraient être également abordées par la théorie.

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